Institute of Physics
of the Czech
Academy of Sciences

Solid State Physics
for 21st century

EXECUTIVE REPORT

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MINISTRY OF EDUCATION,
YOUTH AND SPORTS

Prague, January 17, 2020

Project **"Solid State Physics for 21st Century"** (SOLID21) funded from Operational Program (OP VVV) of EU with the budget exceeding 20 million Euro aims to strengthen the research excellence of the Institute of Physics of the Czech Academy of Sciences (FZU), public research institution, as the leading European centre in the fields of nanoelectronics, photonics, magnetism, functional and bioactive materials and plasma technologies. The mission of the project is to address the most relevant scientific and technological challenges of the 21st century.

The project brings together the best teams of FZU with established research record in key disciplines of solid state physics into a joint focused research centre. The outcome of five cooperating Research Programmes (RP) achieved so far has been briefly summarized in this Report.

As a part of the project, we have started the construction of a new multifunctional building (to be finished in spring 2021) that will provide a versatile space for modern physical laboratories and new scientific facilities, the absence of which has limited further progress at FZU.

The outcomes of the project include new knowledge about electronic, optical and structural processes and energy conversions and storage in nanostructured and modern materials. The gained knowledge will be applied in the development of new electronic, opto-electronic and photonic devices and sensors in physical and chemical sciences, engineering, biology and medicine, corresponding to the key enabling technologies defined by the Research and Innovation Strategy for Smart Specialization of the Czech Republic. Thus the centre is specifically designed to reach out to industry within national and international research and innovation activities and few examples are provided below.

The centre also collaborates with universities to strongly engage students, providing the opportunity to expand and develop their professional skills. Furthermore, extended collaboration with many national and foreign institutions around the globe has already become well evidenced in so far published original papers (above 90 at present). In this way SOLID21 also facilitates the integration of FZU into the European Research Area (ERA).

Research programme Physics for Material Engineering (RP1) – head Oleg Heczko

RP1 consists of five Research Activities (RA) and technical support division.
The program focuses on the research of various ferroic and multi-ferroic materials. It covers the research of modern functional materials with properties achieved through targeted manipulation of microstructure formed by specific phase transformation.

The selected major achievements are summarized below.

RA1&RA2 - Functional ferroelastic materials (P. Šittner) and NiTi shape memory alloys (L. Heller) focus on the basic and applied research of martensitically transforming shape memory alloys. Results of the recently completed and published experimental and theoretical work suggest that coupled martensitic transformation and plastic deformation via dislocation slip and/or deformation twinning play more important role in the mechanics of NiTi deformation then assumed so far. We have showed that ideal fully recoverable shape memory responses can be achieved only under very limited [stress, strain, temperature] conditions, since plastic deformation commonly accompanies martensitic transformation in NiTi, particularly if it proceeds under large tensile stress and elevated temperatures [1]. If the martensite phase is stressed up to the yield stress for deformation twinning in oriented martensite [2] or if the martensitic transformation proceeds at stresses comparable to this yield stress [1], tensile deformation becomes unrecoverable, austenite twins massively appear in the microstructure of deformed alloys. NiTi exhibits TRIP like deformation responses under such conditions that can be understood and predicted

RA2 - Magnetic materials with martensitic transformation (O. Heczko) focuses currently on compounds based on ordered Ni-Mn-Ga, which is the main representative of magnetic shape memory behaviour. Main scientific problem in this field is to understand the anomalous (extremely high) mobility of ferroelastic (twin) boundaries. As an example we listed here the investigation of the interplay between ferroelastic and ferromagnetic domain boundaries with yet another defects – antiphase boundary using high resolution TEM [3] performed in cooperation with University of Carnegie Mellon University in Pittsburgh, USA.

RA4 - Physical research of piezoelectric materials (J. Hlinka) deals with piezoelectric response in various dielectric crystals [4,5]. The group purchased and tested new equipment for multifrequency piezoforce microscopy (PFM) to study ferroelectric domain structures. Several students are involved in the domain engineering activities. In addition, the group was involved in organization of various symposia at the international conferences, e.g. E-MRS or Conference on Electronic Materials and Applications 2019.

RA5 - Multifunctional liquid crystals and composites (V. Novotná) prepared and studied new self-assembling systems, focusing on identifying new effects and deeper understanding of the structure-properties relations. Liquid crystals also became a subject of growing interest as a prosperous medium to induce a self-assembly of nanoparticles. They prepared and studied silver nanoparticles functionalized with ligands based on lactic acid derivatives and proposed a model based on self-assembly of intercalated liquid crystalline ligands [6]. Moreover, they found a facile route how to prepare the nanotubes from organic mesogenic molecules dissolved in typical solvents. The obtained supramolecular assemblies were studied using AFM, TEM and SEM techniques, other experimental techniques (IR, UV-Vis spectroscopy and x-ray diffraction) were also applied. Quite new rolling-up mechanism was proposed related to the surface tension difference at opposite crystallite surfaces. [7] Organic materials with low-dimensional structures such as nanotubes and nanorods can be of great importance in optoelectronics and nanoelectronics.

Summary of the main goals and identification of potential problems in the implementation for the following period (01/01/2020-30/06/2020):

The important part of the project is equipment and capacity investment: The main task of the project is to build-up the new research facility in FZU campus Slovanka. As many of the research team laboratories and personnel are going to move to new premises, the teams were involved in planning and checking the technical arrangement in new building. This is coordinated by the Equipment and technical support (Daniel Šimek). His other main task is to prepare public tenders from technical point of view. The planned investment of Texture diffractometer is in the final stage of the acquisition process. In a public contest (despite some obstacles), the solution of Rigaku Inovative technologies Europe (RITE) was evaluated as the best suitable with delivery price of over 11 mil. Kč. without VAT. The equipment was brought to FZU at 13th December 2019 and is currently undergoing the assembly procedure in temporary premises of Rotan X-ray laboratory. It is expected that the hand-over is going to take place around mid of January 2020 and after initial training it will be in use from the beginning of February 2020 in compliance with the scheduled milestone of the technology (1st quarter 2020). The purchase of major investment X-ray microscope is planned for 2021 to be installed directly in new premises.

There are no foreseeable problems in planned research or the purchase of new research equipment. Planned milestones will be fulfilled. There might be some delay in construction work which can delay the installation of new devices. This we will mitigate by the arrangement on current premises and intensive cooperation.

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Research Program Nanoelectronics (RP2) – head Stanislav Kamba

RP2 consists of five Research Activities (RA):

RA1. Nonlinear optoelectronic and local transport phenomena in semiconductors and semiconductor nanostructures (P. Kužel)
RA2. Control of single-electron charged states in molecules (P. Jelínek)
RA3. Graphene and 2D materials (J. Červenka)
RA4. Magnetoelectric coupling and spin interactions in multiferroic materials (S. Kamba)
RA5. Magnetic anisotropy and magnetization dynamics in nanostructured strongly correlated magnetic materials (A. Shick)

The selected major achievements are summarized below.

1. Publication of a comprehensive review of THz conductivity in nanostructures including conventional semiconductors and carbon-based nanomaterials like graphene and carbon nanotubes. We classified the various regimes of the terahertz response and categorized the available microscopic state-of-the art models including classical and quantum approaches within a unified picture of the behaviour of confined carriers. [1]
2. Development of semiclassical and quantum theory for THz conductivity spectra of charges moving ballistically in one-, two-, and three-dimensional infinitely deep rectangular potential wells. Prediction of a series of geometrical resonances which are coupled with plasmon resonances. [2]
3. Performance comparison of time-domain THz, multi-THz, and Fourier transform infrared spectroscopies. [3]
4. Explanation of nature of binding in planar halogen-benzene assemblies and analysis of their possible visualization in scanning probe microscopy. [4]
5. Near-contact-AFM study of complex azide and nitrene chemistry in UHV on the Ag(111) surfaces with precise determination of the final chemical products. High-resolution imaging of single moleculs was supported by first-principles calculations. [5]
6. Comparative study of catalyst-induced doping and metal incorporation in silicon nanowires. [6]
7. Determination of anisotropic high-frequency dielectric response in polar nanoclusters of relaxor ferroelectrics and discovery of ferroelectric phase transition within the nanoclusters. [7]
8. Discovery of electromagnons in THz spectra of multiferroic $SrMn_7O_{12}$ and their description by a dynamic magnetoelectric coupling. [8]
9. Development of new strained thin films of $(SrTiO_3)_{n-1}(BaTiO_3)_1SrO$ with extremely low dielectric loss and high tuning of permittivity in microwave region, characterization of the films in THz and IR region. This material is highly perspective for 5G mobile networks. [9]
10. Explanation of magnetism in Dy@[Graphene]/Ir(111) was performed using the DFT+Hubbard-I method and good qualitative agreement with experimental results was obtained. [10]
11. Experimental and theoretical (DFT+U) investigation of new neptunium intermetallic compound NpPt2In7. [11]

Summary of the main goals and identification of potential problems in the implementation for the following period (01/01/2020-30/06/2020):

Two large investments are planned within the project. These are Terahertz Scanning Near-field Optical Microscope (THz-SNOM, 637 kEuro) and equipment for Atomic Layer Deposition (ALD, 522 kEuro). Both apparatus have been already ordered and should be installed till summer 2020.

Two milestones (M2.03- Understanding of mobility in nanostructured samples and M2.06- Quantum mechanical theory of charge carrier transport) planned for this term in RA1 have been accomplished in 2019 (see [1,2]). Milestone M2.02 (THz-SNOM in operation) is expected to be executed in spring 2020. RA2 plans to accomplish the milestone M2.09 (Formation of single electron charge states in molecules on surface) and this seems realistic. The installation of ALD setup (M2.13 from RA3) is expected for summer 2020. The milestones M2.21 and M2.22, relative to RA4, (Electromagnons in Y- and Z-hexaferrites), have been completed in 2019. RA5 accomplished the milestone M2.29 (Electronic and magnetic characterization of rare-earth adatoms on Graphene) in 2019 (see [10]).
Finally, we can summarize that most of milestones planned for the next period have already been accomplished and the remaining ones for the next period are well achievable within the planned schedule.
We do not expect any serious problems, if the installation of both apparatus is realized in time.

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Research Program Photonics and energy conversion (RP 3) – head Martin Nikl

RP 3 is composed of five Research Activities:

RA1 - Phosphors for solid state light sources (V. Jarý); **RA2** - New material concepts and technologies of scintillation materials (M.Nikl); **RA3** - Luminescence of nanostructures of silicon and other semiconductors (K. Kůsová); **RA4** - Nanostructures for photovoltaic solar energy conversion (A. Fejfar) and **RA5** - Thermoelectric materials, heat transfer and thermoelectric applications (J. Hejtmánek).

The selected major achievements are summarized below.
We have purchased and installed all the devices according to the project plan and we met the plan of publication output. Few patent applications are pending (RA1, RA2, RA3, RA4).

RA1: A set of multicomponent $ARES_2$: 0.05% Eu sulfides (A = ∑ (Rb, K, Na); RE = ∑ (La, Gd, Lu, Y)) was synthesized creating novel phosphors for solid state lighting technology [1]. Their color-correlated temperatures cover the warm-like 1870 K up to cold-like 5570 K range and high color rendering index can exceed 90. Furthermore, we initiated world-unique µ-PD sulfide single crystal growth experiments.
Optical properties of novel Eu^{2+}-doped garnet phosphors designed for all-in-one RGB technology were measured in order to quantify the influence of Gd^{3+} admixture (into the YAG matrix) on spectroscopy characteristics and explain the nature of emission quenching in ceramics (collaboration with Shanghai Institute of Ceramics).

RA2: Four European projects were finished within this period (H2020 Ascimat, Intelum and TAKEMI5 and COST FAST) and we continue to work in a broad international collaboration. The advanced material concepts of bulk single crystal complex oxide and halide scintillators have been prepared using our novel micro-pulling down technology and classical Bridgman method (halides). Compositions include $(Gd,Lu,Y)_3(Al,Ga)_5O_{12}$ [2], Cs_2HfX_6, $Sr(Hf,Zr)O_3$ and $LaAlO_3$ compounds. Thin films of fast emitting garnet scintillators are also under attention for industrial applications [3]. Preparation and testing of bulk single-crystal and nanocomposite scintillators is carried out also in cooperation with the Crytur company which coordinates two new joint projects awarded in Technology Agency of the Czech Republic from 1/2020.

RA3: We have improved the analysis of the data coming from the experiments of time- and spectrally-resolved photoluminescence [4] and studied new type of excitation energy transfer from Si-nanocrystal to an optically active centrum. We have designed and prepared photonic structure on nanodiamond for resonant excitation and emission extraction which improves its detected intensity more than 100 times. In search of new methods of preparation of luminescencent silicon nanostructures, we have set up a two-stage plasma system with the first stage meant for the synthesis of Si nanocrystals using non-thermal plasma and the second stage for surface passivation in plasma. Preparation parameters leading to luminescent crystalline sub-10-nm silicon cores were found and the function of the second passivation stage was verified using methyl-silane as the passivating agent.

RA4: We have finalized the H2020 project NextBase focused on R&D of high efficiency solar cells with low cost based on silicon wafer heterojunctions with interdigitated back contacts. The project reached close to the world-record high efficiencies of IBC-SHJ on cell (25.4%) and module level (22 %). The technology is ready for mass production in 2020 and will be tested at the project consortium industrial partners. The exploratory research in other types of candidate nanostructures in the modern types of solar cells included Lead Iodide Perovskites, where we have studied their fundamental optical properties [5] or degradation mechanisms [6]. Other type of nanostructures included silicon nanowires (in cooperation with RP2).

RA5: We focused on thermoelectric materials based on non-toxic and abundant elements, mainly n-type sulfides based on antiferromagnetic doped chalcopyrite $Cu_{1-x}Tm_xFeS_2$ (Tm=Pd, Cr, Mn, Fe, Cu…). Challenging physical issues include e.g. the explanation of synergy of antiferromagnetic ground state based on the Fe^{3+}- S network and unusually high electron mobility peaking to ~100 $cm^2V^{-1}s^{-1}$. Ultranano $CuCr_2S(Se)_4$ ceramics represents p-type spin-polarized "metal" and offers practically exploitable thermoelectric potential. Thermoelectric and thermomagnetic studies were focused also onto the intermetalics of $La(Nd)Pt_2Si_2$ type [7] and binary magnetic nanomaterials of the ε-Fe_2O_3 type and iron sulfospinel Fe_3S_4 greigit. Cold isostatic pressing compaction of synthetized powders allows to characterize galvanomagnetic and thermomagnetic properties of highly unstable materials well above room temperature.

Summary of the main goals and identification of potential problems in the implementation for the following period (01/01/2020-30/06/2020):

RA1: We will extend collaboration with Prof. P. Smet (Ghent University, Belgium), the world leading expert in the field of white LED phosphors, aiming to measure quantum efficiencies and energy-dispersive X-ray spectroscopy in SEM at our phosphors. For future developments we also consider the Mn^{4+}-doped oxide hosts for red phosphors.
RA2: More attention will be paid in next period to nanomorphological systems based on direct gap semiconductors (ZnO, GaN-InGaN, lead halide perovskites) which provide possibility for superfast timing (response below 1 ns). Structures include multiple quantum wells, quantum dots and nanocomposites.
RA3: A new surface modification method, based on non-thermal plasma, of the already established porous-silicon-based Si nanocrystals has been developed and will be used in future samples preparation.
RA4: We are going to advance further the optical profilometry developed in the previous period, bringing it to higher TRL and exploring its use. Furthermore, we will start to use the innovative spectroscopic setup for photoresponse measurement, which was installed by the end of 2019.
RA5: Novel and unique technological route based on mechanosynthesis of nanopowders (~10 nm grains), realized in cooperation with the SAS in Košice, will be extensively used.

We do not identify potential problems in the project implementation at present.

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Research Program Physics for bio (RP4) – head Oleg Lunov

RP4 consists of five Research activities (RA):

RA1 - Biophysics of high-gradient magnetic fields (O. Lunov); **RA2** - Plasma and irradiation for bioapplications (A. Dejneka); RA3 - Bioelectronics and biosensors (A. Kromka); **RA4** - Nanoparticles for theranostics (I. Kratochvílová) and **RA5** - Biomaterials and biointerfaces (Š. Potocký).

RP4 devotes its major aim for the establishment of a unique biophysical cluster. The individual laboratories, dealing with those research lines, have started successfully cooperation at both local and international level. Acquisition of modern instrumental equipment has begun: RP4 got unique super-resolution confocal optical system (IXplore SpinSR10, Olympus) giving unprecedented live resolution of lower than 100 nm. Overall, RP4, in collaboration with other RP's, published 40 papers during the reported period from 01/07/2018 to 31/12/2019.

The selected major achievements are summarized below.

RA1: We used pulsed magnetic field for controlled and targeted initiation of lysosomal permeabilization in cancer cells via mechanical actuation of magnetic nanomaterials [1,2]. In this study a benchtop pulsed magnetic system was utilized to remotely activate an apoptosis in liver cancer cells. We showed that liver cancer cells loaded with magnetic nanoparticles can be effectively killed by application of a high intensity (up to 8 T), short pulse width (~15 μs), pulsed magnetic field. Indeed, the magnetic system we designed represents a platform that can be used in a wide range of biomedical applications.

RA2: Biological effects of lasers have been reported for some time, yet the molecular mechanisms procuring cellular responses remain obscure. We showed that mitochondria serve as sub-cellular "sensor" and "effector" of laser light non-specific interactions with cells [3,4]. Our findings reveal the mechanism how laser irradiation interfere with cell homeostasis and underscore that such laser irradiation permits remote control of mitochondrial function in the absence of chemical or biological agents.

RA3: We developed a diamond-based impedance sensor with built-in gold interdigitated electrodes as a promising platform for simultaneous electrical and optical monitoring of the adipose tissue-derived stem cells [5].

RA4: We primarily focused on nanoparticles for drugs, vaccines and diagnostic constructs containing, in addition to functional substances, specific vectors and carriers (liposomes, diamond and magnetic nanoparticles). In [6] we presented the first in vitro study demonstrating direct activation of inflammasome by carbonylated nanodiamond.

RA5: We reviewed the fabrication of various porous diamond-based structures using linear antenna MW plasma chemical vapor deposition, a low-cost technology for growing diamond films over a large area (>1 m^2) at low pressure (<100 Pa) and at low temperature (350°C). Two different approaches, i.e., templated diamond growth on prestructured (macro-, micro-, and nano-sized) porous substrates and direct bottom-up growth of ultra-nanoporous diamond films, were successfully used and optimized [7].

Summary of the main goals and identification of potential problems in the implementation for the following period (01/01/2020-30/06/2020):

RA1: Physical and biological understanding, in molecular terms, of the response of cultured cells to magnetic nanomaterials and effects of high-gradient magnetic fields exposure.
RA2: A deeper understanding of the mechanism of action of plasmas and irradiation on cell, bacterial cultures and live tissue.

RA3: Optimization of technological processes of diamond and carbon based bio-electronic devices.
RA4: Investigation of microfluidic mixing technique for preparation of liposomes and lipid-based nanoparticles by on-chip technologies which are applicable in laboratory and industrial scale. The biological part of the research will focus on the detailed study of interactions with cells and subcellular compartments (extent of internalization and particle distribution in cells).
RA5: Study of cells cultivation on substrates with various morphologies and topography.

We are conscious of the complexity of the stated objectives in this project phase. Specifically, concerning usage of complicated methodologies for material characterization and their implication into in vitro cell culturing. However, the collaboration of specialized entities in the Institute of Physics allows us to be confident of success.

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Research program Plasmatic Technologies (RP 5) – head Zdeněk Hubička

RP5 is composed of six Research activities (RA):

RA1- R&D of advanced low temperature plasma systems for thin film polycrystalline materials (Z. Hubička); **RA2** - Plasma diagnostics, optimization of plasma deposition systems, and monitoring of deposition processes (M. Čada); **RA3** - Plasma methods of preparation of thin metallic and intermetallic layers (J. Lančok); **RA4** - Thin-film chemical sensors (M. Novotný); **RA5** – Optical materials-plasmon structures (J. Bulíř) and **RA6** – Structures exhibiting a combination of ferromagnetic properties (M. Tjunina).

The selected major achievements are summarized below.

RA1: The research was oriented on the development of new low-temperature plasma system suitable for the deposition of metallic and dielectric thin films on 3D objects in cavities and long tubes. The CZ patent was approved for this new method and extended on the international patent priority (PCT) [1]. This method combines a pulse hollow cathode discharge combined with a RF plasma generated inside the tube for PVD deposition process. This new system was applied for the deposition of Co_3O_4 catalytic films with the large active area [2] The reactive HiPIMS system combined with the ECWR plasma was applied for the deposition of copper oxide semiconducting thin films with p-type conductivity. Photoelectrochemical parameters were investigated on these films prepared on FTO glass [3] The system was currently extended on two reactive HiPIMS magnetron system and ternary photoactive semiconducting oxides based on $CuFeO_2$ were prepared with the p-type conductivity.

RA2: Physical processes were investigated in the reactive HiPIMS plasma system during the deposition of various oxide semiconducting thin films. The most important results were published [4,5].

RA3: We have focused on the research of thin films of Heusler alloys in cooperation with VP1. The electronic structure and twinning in the martensitic phase of Ni-Mn-Ga Heusler alloy determined by theory and experiment was studied and published in [6]. Research in this area also brought new cooperation with the Charles University in Prague in frame of magnetooptics materials.

RA4: We have focused on the investigation of black metals growth by magnetron sputtering. We used these coating as a light absorber for pyroelectric energy harvesting [7].

RA5: Our attention was focused on in-situ ellipsometer characterisation of the initially growth process of nitrides such as ZrN and TiN films by means of RF magnetron sputtering of metallic target in a reactive nitrogen ambient with respect to plasmonic properties in near infrared region.

RA6: Oxygen vacancy related defects were studied by investigation of optical constants in a broad spectral range of 0.75–8.8 eV in epitaxial ferroelectric BaTiO3 films and results were published in [8].

Summary of the main goals and identification of potential problems in the implementation for the following period (01/01/2020-30/06/2020):

We will finish the tender for the plasma system for the deposition of sulphide and selenides thin films. Further goal is to complete the tender for Laser-MBE deposition system with integrated RHEED system for fabrication of epitaxial thin films.

The research will be oriented on the reactive HiPIMS system and the control of physical processes during the growth of semiconducting thin films. The physics of hybrid HiPIMS+ECWR plasma will be further investigated for very thin film multilayer structures.

The physics of bipolar HiPIMS system will be investigated by very specific diagnostic tools like capacitive probe, ion mass analyser, RF planar probe.

The research will continue in the direction of thin films deposition with outstanding magnetic and magnetooptic properties using the method of DC magnetron sputtering from multiple targets in the UHV system. Epitaxial RhMnSb layers with tetragonal crystal structure as well as Co2TiSn were already prepared on MgO substrates and in cooperation with RP1, the magnetic properties of these materials will be studied.

Some milestones of the project connected with new experimental systems implementations were postponed due to the planned delay of realization on new building. These delays should not have any strong impacts on the realization of scientific program of RP5.

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