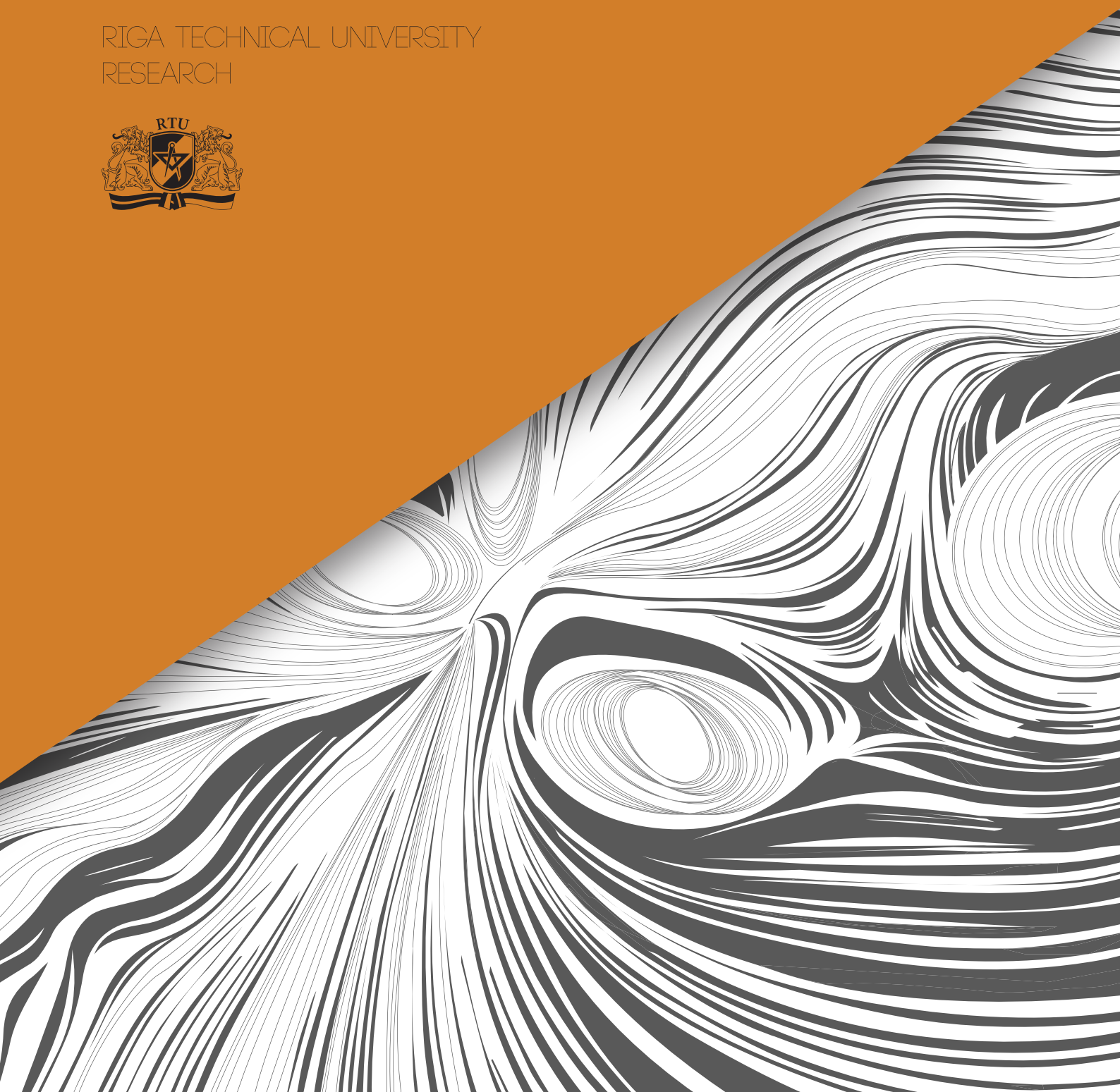
03

MATERIALS, PROCESSES AND TECHNOLOGIES

RIGA TECHNICAL UNIVERSITY
RESEARCH



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03

Dear Reader,

I have the pleasure of introducing you to the third edition that is dedicated to one of six RTU research platforms: Materials and Technologies. In assessment of European experts, just the material science was recognized as one of strongest research fields in Latvia. Work of RTU scientists is an important motive force of this sphere, especially in studies associated with the application of composite materials in transport, use of biomaterials in medicine and utilization of production waste in environmental clean-up.

In historical perspective of this sphere, we can be proud of both Nobel Prize winners and close collaboration with Latvian pharmacological and other enterprises associated with chemistry and material science.

Modern material science field has become an actually interdisciplinary sphere; it is closely connected with the subject of the second volume: the technologies, being an identifying sign of RTU.

Wishing you an interesting reading,

Riga Technical University
Dr. sc. ing., Professor ***Tālis Juhna***
Vice-Rector for Research

MATERIALS, PROCESSES, TECHNOLOGIES

Today synthesis of nanomaterials and their use in obtaining the intelligent materials and products, the modification of traditional materials and extension of their application scope, strength and safety forecasting for materials and constructions, and other materials-related studies are undoubtedly one of the world priority directions in research activities and practical application. This priority development line is also introduced in 3 platforms of BIRTI further activity established in the Baltic countries: BioFarmAliance, NanoTechEnergy and BaltSmartTech, acronyms of which need no comments. RTU scientific activity development strategy put forward five priority research directions, one of which is "Materials, processes and technologies". Today, studies in this field are carried out by all RTU faculties, if maybe not directly but subordinately anyway, developing the data processing, design and forecasting software, performing economic estimates and substantiations for the design and manufacturing technology of new materials. Judging by the definition that the materials are simple or compound substances, mixtures thereof, heterogeneous compositions of natural and synthetic origin, it becomes obvious that the synthesis of materials and their technological processes are an immeasurably broad field for research, which is still further extended by studies associated with a targeted building of materials structure, manufacture of products and constructions for specific objectives and operating conditions. It is almost impossible to list the directions of studies carried out in RTU in this field. They cover a wide range of research from the nanoparticles synthesis and use up to the estimates of large, practically used structures, tests of structural strength and sustainability forecasting.

Without going into details, the main research directions in materials synthesis, study and application can be grouped into the following items:

- *nanomaterials synthesis and use for manufacture of intelligent materials and specific products, for modification of properties of existing materials,*
- *materials for electronics, photonics, optoelectronics and information technologies,*
- *increase in safety and strength of traditional materials and constructions, extension of their scope of use,*
- *optimization of production processes of materials and constructions from the standpoint of energy and resource saving,*
- *extended use and modification of secondary raw materials,*
- *development of environment-friendly and economical materials and technological processes.*

Studies in the sphere of materials, processes and technologies already for a long time are not a field for activity of a single RTU structural unit. Cooperation between RTU institutes and faculties, other research institutions in Latvia and abroad has become an everyday form of collaboration, but it should become even wider and more diversified, especially in the context of Latvian production development. Studies in the field of materials are carried out as the National Research Programmes, research cooperation projects, EU Framework Programmes, ERDF co-financed projects and other formats, solving problems actual for both Latvia and EU. RTU participation in the establishment and activity of four nationally important research centres made it possible to create a high-value modern infrastructure, providing the researchers with world-class scientific equipment, thus promoting an equivalent competition on the global research market and allowing to become equivalent partners of foreign colleagues in international projects. This magazine only overviews some of subjects in the abovementioned priority direction, which are addressed in 4 faculties:

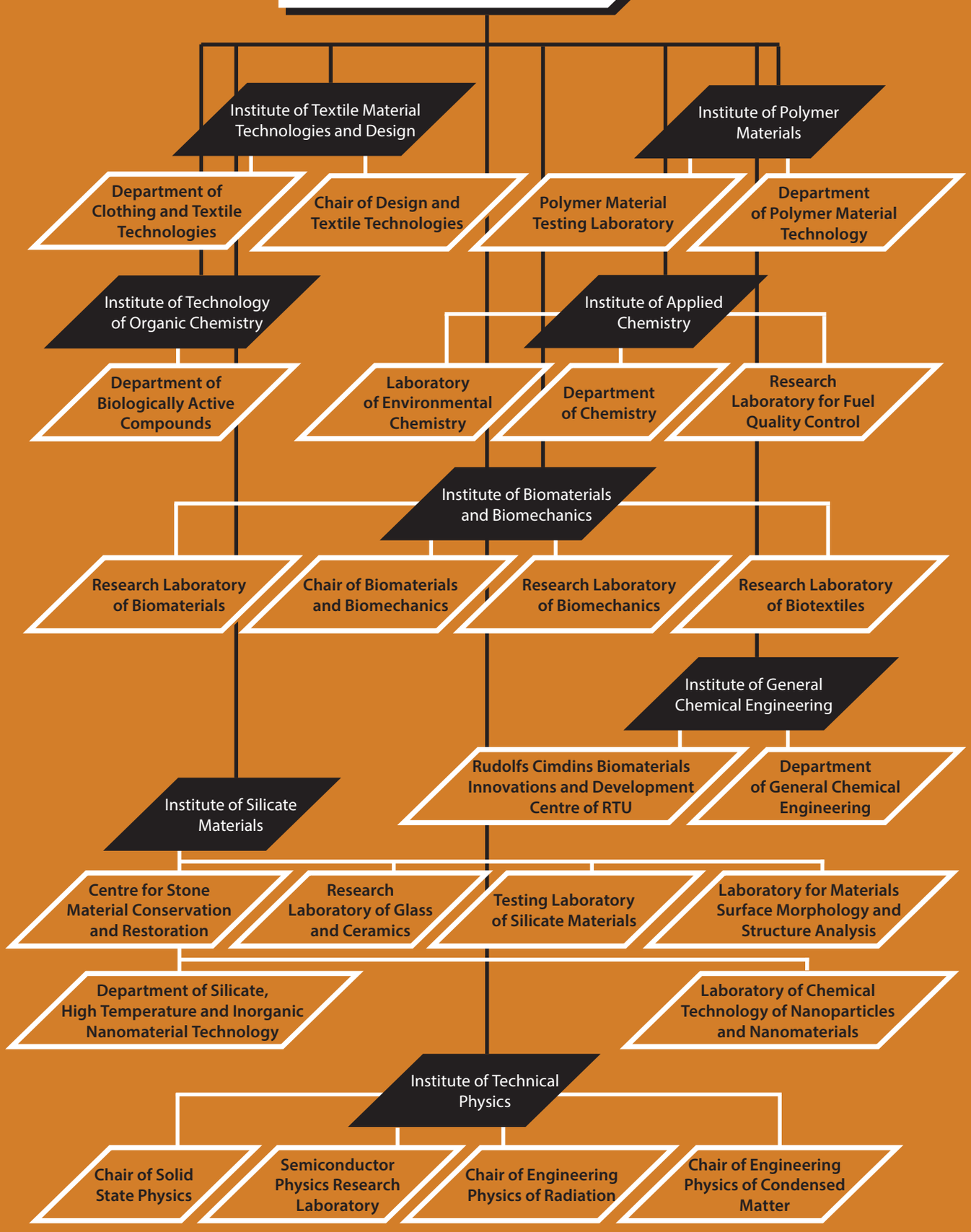
- *insight in development of nanotechnology in Latvia in the context of the European Union,*
- *modification of materials surface and structure on nanoscale level,*
- *creation of special functional materials, including making them from nanomaterials or modifying them with existing materials,*
- *optimization of materials consumption and constructive solutions for manufacture of complex products,*
- *materials for creation of new energy sources, energy-saving solutions and their provision in technological processes of material production and for other purposes,*
- *use of Latvian natural mineral — clays, including in the form of nanoparticles, in cosmetics, water treatment, etc.*

We hope much that the reader, having been acquainted with the content of this magazine, will acquire a certain insight into directions and possibilities of our studies; that the interest will be aroused among manufacturers, foreign scientists or simply readers, which would be an incentive for further RTU cooperation and studies.

Faculty of Material Science
and Applied Chemistry
Dr. sc. ing., Assoc. Prof. ***Mārcis Dzenis***
Deputy Dean for Research

CONTENTS

FACULTY OF MATERIAL SCIENCE AND APPLIED CHEMISTRY



VISIBLE LIGHT ACTIVE MULTI-COMPONENT PHOTOCATALYSTS FOR ENVIRONMENTAL REMEDIATION

***Faculty** of Material Science and Applied Chemistry*

***Institute** of Silicate Materials*

►Dr. sc. ing.
Andris Šutka

ABSTRACT

Photocatalytic water purification under irradiation by sunlight has received much attention due to environmental remediation. Efficient use of visible light is one of the greatest challenges in science and requires the development of visible light responsive photocatalysts with high efficiency. To provide abroad visible light absorption and high visible light photocatalytic efficiency, we have developed novel two- and three-component visible light active photocatalysts greatly increasing the visible light absorption and decreasing the electron-hole recombination rate. Besides, in our studies we coupled a wide band gap TiO_2 photocatalyst with spinel ferrites, which exhibit also ferrimagnetic or superparamagnetic properties enabling a simple recycling of photocatalyst nanopowders by use of a magnetic field.

***Keywords**: photocatalyst, multi-component, heterostructure, visible light.*

INTRODUCTION

The widespread organic and toxic environmental pollution has surpassed the threshold of natural purification and has become an urgent task that needs to be accomplished. Semiconductor photocatalysis is one of the most perspective futuristic wastewater and air treatment solutions for environmental remediation. Semiconductor photocatalysis is a "green" advanced oxidation non-energy process for the complete mineralization of pollutants. There are several advantages of the semiconductor photocatalysis, such as low process temperature, high efficiency and low cost. Semiconductor photocatalysts can be used also for (i) mimicking overall natural photosynthetic cycle to obtain hydrocarbon fuels by photocatalytic reduction of CO_2 with H_2O, thus saving the environment and (ii) water splitting to obtain H_2 fuel by conversion of solar energy into chemical energy, which represents a promising technology to overcome the energy shortage. It is suggested that hydrogen production by means of photocatalytic water splitting may cover one-third of the energy needs of human society in 2050. Figure 1 shows possible scheme for large-scale H_2 production via solar water splitting.

Semiconductor photocatalysis is generally based on the light absorption of semiconductor oxides when energy of the incident photons matches or exceeds the bandgap. In its simplest form, semiconductor oxide nanopowders are dispersed in wastewater and the suspension is exposed to light irradiation. The absorbed photons excite the electrons to the conduction band and leave a hole in the valence band of semiconductor oxides, thus creating the photogenerated electron-hole pairs, which, in turn, trigger reduction and oxidation reactions in

the presence of irradiated semiconductors. Figure 2 shows a schematic illustration of basic mechanism of semiconductor photocatalytic process. Generally, photocatalysis involves three processes: charge carrier excitation, bulk diffusion and surface transfer.

To date, the TiO_2 and ZnO semiconductor oxide photocatalysts have undoubtedly proven to be the most excellent materials for photocatalytic process due to high photosensitivity and high charge carrier mobility, leading to enhanced water splitting and the oxidative decomposition of many organic compounds. However, due to their wide band-gap (>3.2 eV), ZnO and TiO_2 do not absorb visible light and can only be excited by ultraviolet radiation, which occupies only 4 % of the incoming solar light spectrum. The efficient use of visible radiation region (>400 nm), which covers around 40 % of the solar spectrum, is one of greatest challenges in science and requires the development of visible light active photocatalysts. Many research works relating to visible light active photocatalysts have been already reported. Visible light photocatalytic activity has been demonstrated by various simple and complex oxides, such as Ag_2O, Bi_2O_3, Fe_2O_3, WO_3, $ZnFe_2O_4$, $NiFe_2O_4$, Bi_2WO_6, as well as doped ZnO and TiO_2 oxides. However, there are still several shortages hindering practical applications of visible light active photocatalysts, such as high recombination rate of photogenerated electron-hole pairs. To enhance the photocatalytic efficiency, it is of crucial importance to suppress the recombination of photogenerated electron-hole pairs. One of the most effective strategies to decrease the recombination and improve the photocatalytic efficiency is heterostructure formation by coupling the semiconductor oxides with metal and/or other semiconductors to form two- or three-component heterostructures. Depending on the charge carrier transfer mechanism, three main heterostructure modes can be distinguished: (i) semiconductor-semiconductor, (ii) semiconductor-metal, (iii) semiconductor-metal-semiconductor (direct Z-scheme). We have developed novel two- and three-component visible light active photocatalysts that greatly decrease the electron-hole recombination probability. Besides, in our studies we coupled a wide band gap TiO_2 photocatalyst with spinel ferrites, having not only broad visible-light absorption range, but also possessing ferrimagnetic or superparamagnetic properties. Magnetic properties enable simple recycling of photocatalyst nanopowders from treated waste water by use of magnetic field.

TWO-COMPONENT TIO_2 – NICKEL FERRITE HETEROSTRUCTURES

Direct coupling of semiconductors to obtain two-component heterostructures requires finding suitable semiconductors with proper band edge positions and intimating contact between the two phases. Proper band edge positions means that the valence and conduction band potentials of one semiconductor should be more cathodic (more negative) than those of other semiconductor to provide an effective separation of photogenerated charge carriers between coupled semiconductors. Schematic representation of the charge carrier separation in two-component heterostructure is shown in Figure 3.

To impart visible light photocatalytic activity, we have synthesized heterostructures where anatase TiO_2 is coupled with nickel ferrite ($NiFe_2O_4$). $NiFe_2O_4$ was chosen for these studies due to its suitable properties. $NiFe_2O_4$ has a narrow band-gap (1.56 eV) attributed to the optical transition from d–d type orbitals, and its conduction potential (−1.62 VSCE) is more negative than that of TiO_2 (−0.5 VSCE), which is necessary for creating the potential gradient at the two-semiconductor interface. The spinel-type compounds, such as $NiFe_2O_4$, also show an excellent chemical and photo-corrosion stability, as well as exhibit ferrimagnetic properties due to the uncompensated spins of nickel cations located in the octahedral site of the $NiFe_2O_4$ inverse spinel structure. Figure 4 shows TEM images of commercial TiO_2 anatase nanoparticles before (a) and after (b) $NiFe_2O_4$ coupling.

The photocatalytic activity experiments revealed a significantly improved visible light photocatalytic efficiency, up to three times higher compared to pure anatase or $NiFe_2O_4$, which can be attributed to heterostructure formation and efficient charge carrier separation properties. The charge carrier separation occurred due to electron migration from the conduction band of narrow band gap semiconductor to the conduction band of wide band gap semiconductor and the hole migrates from the valence band of wide band gap semiconductor to the valence band of narrow band gap semiconductor. The obtained semiconductor heterostructures may have a potential application in the field of photodegradation of organic pollutants.

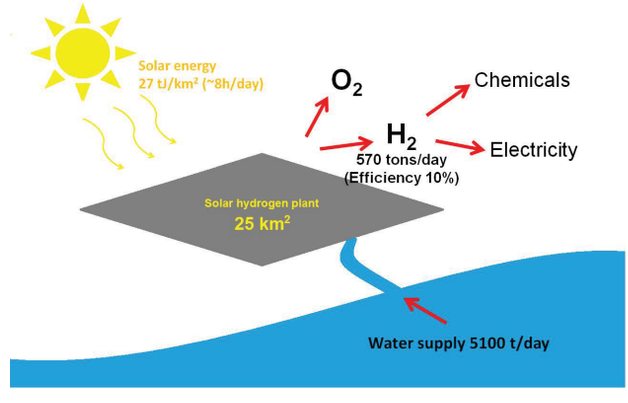


Fig. 1. *Large-scale H_2 production via solar water splitting. 10,000 solar plants (each of 25 km² area) would be required to provide one-third of the projected energy needs of human society in 2050 from solar energy.*

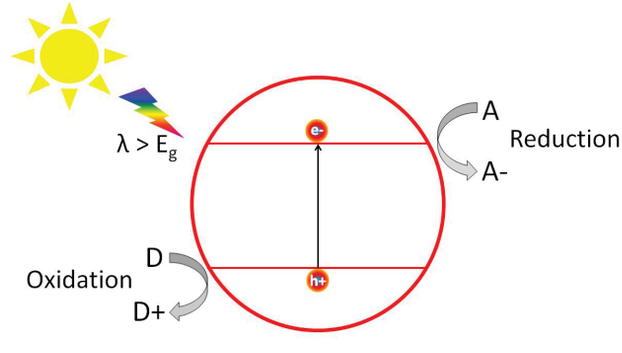


Fig. 2. *Schematic illustration of a semiconductor photocatalytic process.*

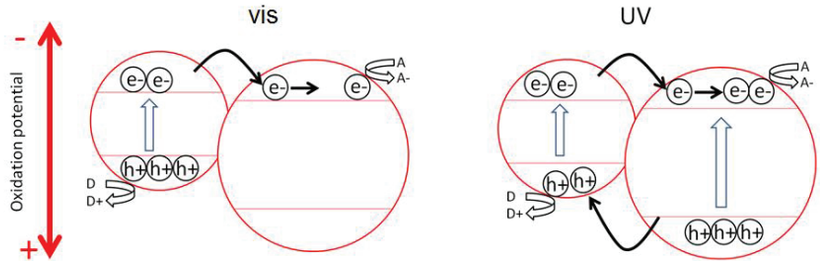


Fig. 3. *Schematic representation of the charge carrier separation in two component heterostructure where narrow (smaller sphere) and wide (larger sphere) band gap semiconductors are coupled. Figure shows charge carrier separation mechanism under visible (vis) and ultraviolet (UV) light irradiation.*

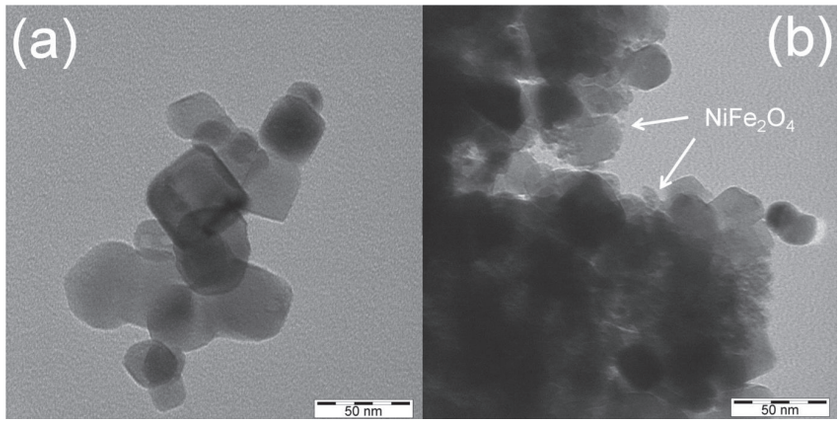


Fig. 4. *TEM images of commercial TiO_2 anatase nanoparticles before (a) and after (b) $NiFe_2O_4$ coupling.*

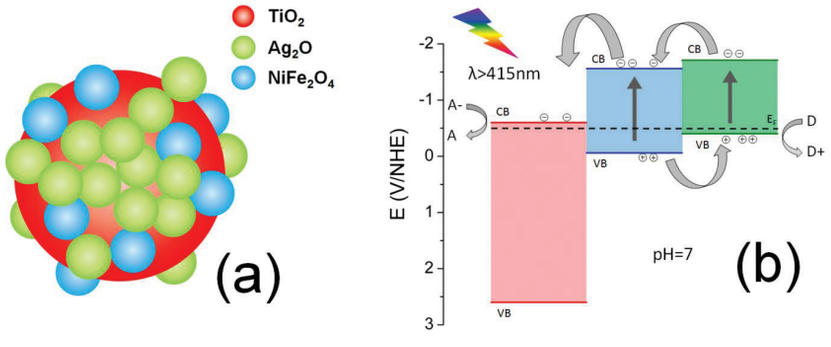


Fig. 5. *Schematic representation of three component semiconductor oxide $TiO_2/Ag_2O/NiFe_2O_4$ heterostructure particle (a) and electron-hole separations and energy band matching of the $TiO_2/Ag_2O/NiFe_2O_4$ heterostructure under visible light irradiation*

THREE-COMPONENT TIO_2 BASED HETEROSTRUCTURES

In spite of numerous research works relating to the visible light responsive photocatalysts, investigations devoted to the alternative materials and synthesis or modification techniques of existing materials to provide broad visible light absorption and high visible light photocatalytic efficiency are still important. To enhance the charge carrier separation and to broaden the photoabsorption range, multicomponent heterostructure systems have been developed. Typical multicomponent heterostructures consist of two coupled semiconductors and metallic intermediate layer between them. Such type of three-component heterostructure is called an all-solid-state Z-scheme due to realization of biomimetic Z-scheme charge transfer mechanism observed in the natural photosynthesis system. Transferred electrons and holes recombine in metal intermediate layer and thus holes in wide band gap semiconductor are effectively separated from electrons in narrow band gap semiconductor.

Recently, we had shown other type of multicomponent semiconductor heterostructure in which three oxides TiO_2, Ag_2O and $NiFe_2O_4$ were coupled. It was found that three-component heterostructure formation between TiO_2, Ag_2O and $NiFe_2O_4$ oxides was energetically favourable for photo-induced charge carrier separation due to band matching between three oxide components (see Figure 5). Anatase TiO_2 has the highest band-gap energy (3.2 eV) and most positive conduction-band potential (−0.5 VSCE at pH = 7). $NiFe_2O_4$ has a band-gap energy of 1.56 eV and conduction-band edge positioned at −1.62 VSCE (pH = 7), while Ag_2O has the narrowest band-gap at −1.3 eV and the most negative conduction band edge (−1.7 VSCE at pH = 7). Energetically favourable three-component heterostructure formation suppressed the rate of electron hole recombination due to effective photogenerated charge carrier separation. The synthesized three-component heterostructure showed a superior photocatalytic efficiency destroying 100 % of the methylene orange (10 mg/l) in water during 2 h irradiation under visible light.

CONCLUSIONS

This report presented the fundamental aspects of semiconductor photocatalysts for environmental remediation, as well as gave a short tutorial on our recent achievements on this topic. Briefly, to provide broad visible light absorption and high visible light photocatalytic efficiency, we have developed novel two- and three-component visible light active photocatalysts, which greatly increase the visible light absorption and decrease the electron-hole recombination rate. Two- and three-component anatase based systems have been successfully obtained by wet-chemical synthesis, such as photodeposition and co-precipitation. It was found that two- and three-component photocatalytic systems exhibited significantly enhanced photocatalytic activity compared to single components.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the European Social Fund project "Elaboration of Innovative Functional Materials and Nanomaterials for Application in Environment Control Technologies" No. 1DP/1.1.1.2.0/13/APIA/VIAA/30.

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KOPSAVILKUMS

Apkārtējās vides attīrīšana, izmantojot pusvadītāju fotokatalizatorus, ir viena no perspektīvākajām nulles enerģijas metodēm un šī iemesla dēļ iegūst arvien lielāku nozīmi. Pētījumu gaitā iegūtas nanoizmēra cietvielu heterostruktūras, kurām redzamajā gaismā piemīt augsta fotokatalītiskā aktivitāte. Viens no fotokatalizatoru augstas aktivitātes priekšnosacījumiem ir augsta gaismas absorbcija. Līdz šim augstas aktivitātes fotokatalizatri absorbēja gaismu UV diapazonā, tādēļ to izmantošanai bija nepieciešama papildus enerģija, lai darbinātu UV gaismas avotu. Pētījumu gaitā iegūtajiem nanoizmēru cietvielu heterostruktūru fotokatalizatoriem piemīt augsta redzamās gaismas absorbcijas spēja, tie ir aktīvi saules gaismā un darbojas kā aktīva komponente piesārņotā ūdenī, sadalot videi kaitīgos ķīmiskos savienojumus. Iegūti arī magnētiski fotokatalizatori, kas ir aktīvi redzamajā gaismā un atdalāmi no reakcijas vides ar magnētiska lauka palīdzību.

RESEARCH AND DEVELOPMENT OF ADVANCED BIOMATERIALS: FROM CONCEPT TO CLINIC

***Faculty** of Material Science and Applied Chemistry*

***Institute** of General Chemical Engineering*

***Rudolfs Cimdins** Riga Biomaterials Innovations and Development Center*

►Dr. sc. ing. Prof. ***Līga Bērziņa-Cimdiņa***

►Dr. sc. ing. ***Zilgma Irbe***

►Dr. sc. ing. Assoc. Prof. ***Jānis Ločs***

►Mg. sc. ing. ***Līga Stīpniece***

►Dr. sc. ing. ***Kristīne Šalma-Ancāne***

►Mg. sc. ing. ***Arita Dubņika***

►Dr. sc. ing. ***Dagnija Loča***

►Mg. sc. ing. ***Inga Narkevica***

INTRODUCTION

Musculoskeletal diseases and disorders, such as osteoporosis, osteonecrosis and degenerative osteoarthritis, affect hundreds of millions of people across the world. These bone diseases often lead to bone fragility and complex fracture. The most promising biomaterials for bone tissue replacement and regeneration are calcium phosphates (CaP), especially hydroxyapatite and β-tricalcium phosphate, due to their unique properties — biocompatibility, bioactivity and osteoconductivity [1]. Titanium dioxide (TiO_2) also can be used as a bone substitute, especially in tissue engineering as 3D scaffolds that could bond to living bone and enhance the vascularisation after implantation. Nevertheless, TiO_2 shows a good bioactivity and has a certain degree of bacteriostatic effect [2].

Rudolfs Cimdins Riga Biomaterials Innovation and Development Centre (RCRBIDC) of Riga Technical University performs the multidisciplinary steps of the calcium phosphate and titanium oxide-based biomaterials development process for specific application in living system or functioning in intimate contact with living tissue, and has made significant contributions to the health and quality of human life. The overall goal of our research work is to obtain calcium phosphate bioceramics or their composites which would ensure faster and more efficient recovery of the damaged bone by decomposing into the environment of body and gradually releasing ions or drugs able to affect the bone diseases and regeneration process. Our research group also works on creation of novel 3D titaniabone scaffolds with enhanced bioactivity for biomedical application to solve a public health issues affecting peoples with musculoskeletal problems.

RCRBIDC and Riga Stradins University have long-standing scientific cooperation for evaluation of these materials in pre-clinical studies: *in vitro* and *in vivo,* as well in clinical use, mainly in oral and maxillofacial surgery, started also in orthopaedic surgery. Working closely with clinical and commercial partners enables the work to be approached from broadly based fundamental, clinical and commercial viewpoints. On the basis of in-depth research of calcium phosphates, calcium phosphate bone cements, bioceramic matrices for controlled drug delivery and bioceramics with controlled micro- and macroporosity are developed [3, 4, 5, 6]. Currently several national and international research projects are running in RCRBIAC:

- FP7 EURONANOMED II ERA-NET "Nanoforosteo" "Multifunctional injectable nano HAp composites for the treatment of osteoporotic bone fractures" 2013–2016.
- FP7 M-era.NET „GoIMPLANT" „Tough, Strong and Resorbable Orthopaedic Implants" 2013–2015.
- FP7 MATERA — ERA-NET „SONOSCA" MATERA/BBM-2557 „Sonochemical technology for bioactive bone regeneration scaffold production" 01.01.2012–12.12.2014.

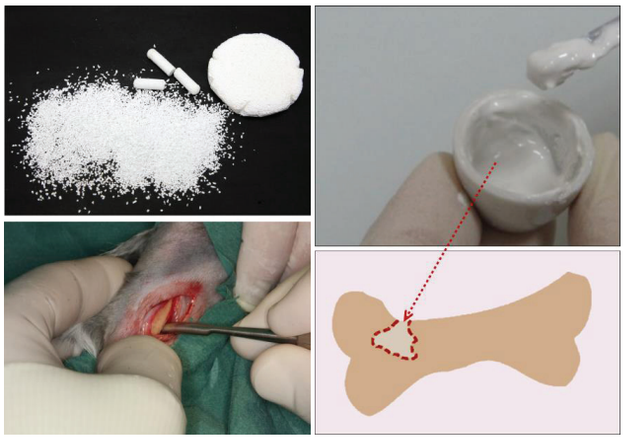

Fig. 1. *Developed calcium phosphate biomaterials for specific application*

DEVELOPMENT OF CALCIUM PHOSPHATE BASED BIOMATERIALS

An effective calcium phosphate multiphase synthesis technology was developed to obtain bioceramics (with controllable ratio of hydroxyapatite/β-tricalcium phosphate phase composition), which demonstrated a good perspective for manufacture of bioceramic implant materials with predictable composition and structure [7].

Selecting and/or combining hydroxyapatite and β-tricalcium phosphate, the biodegradation kinetics of biphasic calcium phosphate bioceramics can be tailored, as well as their stimulating effect on bone formation [1, 8]. Calcium phosphates biomaterials have been developed in the form of dense or porous blocks, sintered granules or polymer composites for application in maxillofacial, dental and orthopedic surgery [4, 5, 9]. To modify the properties of CaP biomaterials, they have been combined with various drugs, such as analgesics, antibiotics or anti-inflammatory substances [3, 6]. Also an increased interest is aroused in the modified synthetic calcium phosphates involving the modifications of ions found in natural bone (i.e. Mg, Sr, Zn, Si). Incorporation of bioactive metallic ions into calcium phosphate structure is important for a number of reasons, including a better understanding of biomineralization process, the increase in bioactivity of material, and ion delivery able to affect the bone diseases [10, 11]. Furthermore, CaP biomaterials can be doped with silver ions, thus obtaining the materials with antimicrobial properties [4, 12, 13].

DEVELOPMENT OF TITANIUM DIOXIDE SCAFFOLDS FOR BONE DEFECT REGENRATION

Biocompatible ceramics have recently attracted an increasing attention as porous scaffolds that stimulate and guide the natural bone regeneration. Due to excellent biocompatibility of TiO_2, porous three-dimensional TiO_2 structures have been proposed as promising scaffolding materials for inducing the bone formation from the surrounding environment [14]. Modifying several important issues that have been considered important for 3D scaffolds applied to bone tissue regeneration, including the surface chemistry, the size and distribution of pores, and the relationship between mechanical strength and porosity of titania scaffolds, can improve cell attachment, vascularisation and bone ingrowth. Scaffolds also must show mechanical properties similar to natural bone, and studies have shown that ultra porous titania scaffolds have much higher mechanical properties compared to other ceramic biomaterials, *e.g.* hydroxyapatite, glass ceramic, but its bioactivity is poor. On the other hand, nanostructured titania coatings have showed excellent bioactivity. Bioactive materials form bonelike apatite layer on their surfaces and bonds to living bone

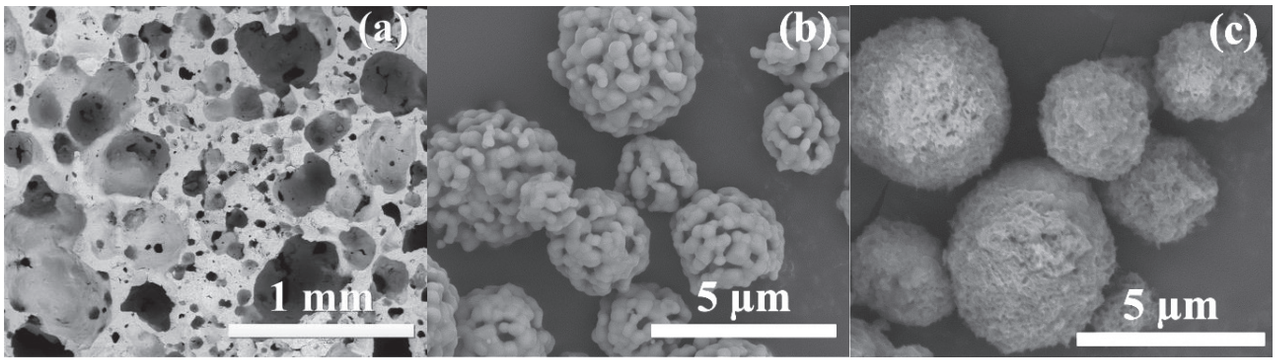

Fig. 2. *Porous blocks (a), sintered granules (b) of calcium phosphates and hydroxyapatite/polymer composite microgranules (c)*

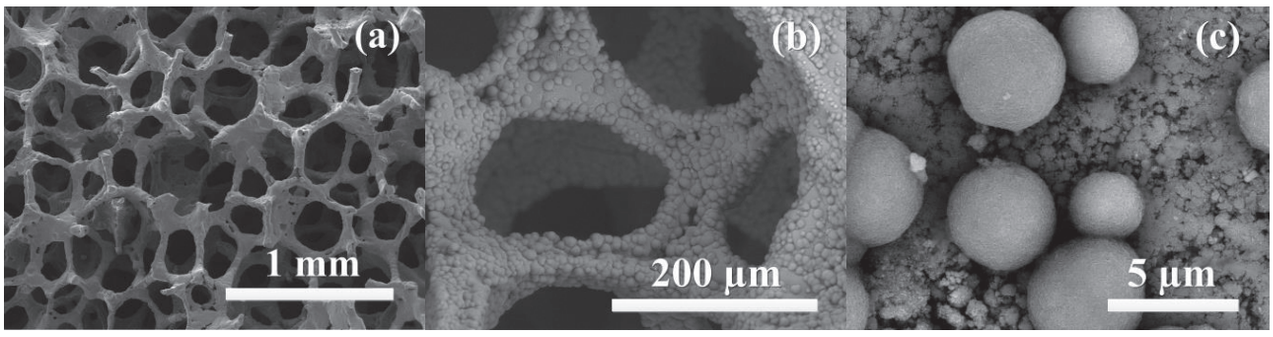

Fig. 3. *Porous TiO2 scaffolds (a), bonelike apatite formed on surface of bioactive scaffolds (b) and dense pellets (c)*

through it. Thus, the ability to induce formation of bonelike apatite on artificial bone implants in human body is vital for successful bonding between the implants and the bone tissue. The accelerated rate of apatite formation is important and will benefit recovery after surgery since the implant should afford earlier load bearing after implantation. Thus combining 3D porous structure of titania scaffolds with nanostructured titania coating can greatly enhance bioactivity. Creation of nanosized surface topography also may result in special and advantageous properties of biomedical implants in a biological environment and, as a result, improve bone defect regeneration. Nevertheless, surface chemistry of such material, *e.g.* surface energy, hydrophilicity, can be easily modified by UV-light irradiation to tailor the cell attachment [3].

CONCLUSIONS

So far, the goal of synthesizing Mg-containing calcium phosphates with various phase and chemical compositions through the wet chemical precipitation has been achieved. Currently, efforts are underway to development of Sr-containing calcium phosphates. The effort of current research is also put on production and characterization of 3D porous titania scaffolds with interconnected pore structure and nanostructured titania coating for bone tissue engineering. Developed multidisciplinary cooperation from "laboratory to clinics" provides not only the joint use of unique scientific infrastructure and scientific knowledge, but also opens the new horizons for the preparation of novel biomaterials for bone tissue engineering strategies.

ACKNOWLEDGMENTS

Part of this work has been supported by the European Social Fund within the project "*Involvement of new scientist group for synergistic investigation to development of nanostructured composite materials for bone tissue regeneration*", No. 2013/0007/1DP/1.1.1.2.0/13/APIA/VIAA/024.

Part of this work was supported by the European Social Fund within the project "*Multidisciplinary research in biomaterials technology of new scientist group*", No. 2009/0199/1DP/1.1.1.2.0/09/APIA/VIAA/090.

ESF EIROPAS SOCIĀLAIS FONDS IEGULDĪJUMS TAVĀ NĀKOTNĒ EIROPAS SAVIENĪBA

Part of this work has been supported by the European Social Fund within the project "*Support for the implementation of doctoral studies at Riga Technical University*".

Part of this work was supported by the National Research Program of Latvia in Material Sciences No. 2 "Development of novel multifunctional materials, signal processing and information technologies for competitive knowledge-based products — IMIS" project No. 4 "N*ovel materials and technologies for implantation and evaluation of biological tissues*" (2010–2014).

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KOPSAVILKUMS

Rīgas Tehniskās universitātes Vispārīgās ķīmijas tehnoloģijas institūta Rūdolfa Cimdiņa Rīgas Biomateriālu inovāciju un attīstības centrā jau vairākus gadus tiek veikts sistemātisks pētnieciskais darbs, lai izstrādātu jaunus, inovatīvus funkcionālus kalcija fosfātu un titāna oksīdu saturošus biomateriālus, kas paredzēti kaulaudu aizvietošanai un kam piemīt specifiskas atjaunojošas, kaulu slimību aizkavējošas īpašības. Sadarbībā ar Rīgas Stradiņa universitāti tiek veikts apjomīgs eksperimentālais darbs, lai izstrādāto kaulu implantmateriālu aprobētu *in vitro* un *in vivo,* kā arī klīniskajās studijās. Šobrīd tiek turpināts darbs pie jaunu tehnoloģiju izstrādes, lai iegūtu blīvu un porainu biokeramiku, porainas keramiskas granulas, kā arī polimēru kompozītu formas, kas būs izmantojamas mutes, sejas un žokļu ķirurģijā, rekonstruktīvajā ķirurģijā un ortopēdijā. Tiek pētīta organismam labvēlīgu neorganisku, bioloģiski aktīvu elementu — stroncija un magnija — iekļaušana kalcija fosfātu struktūrā. Variējot jonu aizvietošanos kalcija fosfātu kristāliskajā struktūrā, ir iespējams kontrolēt to fizikāli ķīmiskās īpašības, kā arī bioloģisko saderību un bioaktivitāti. Zinātnieku nākotnes uzdevums ir pielāgot kalcija fosfātu sastāvu, mikrostruktūru un molekulāro virsmas ķīmiju specifiskām audu bioloģijas un metabolisma prasībām, kā arī dažādām kaulu slimību stadijām.

THERMOELECTRIC PROPERTIES OF TIO_2 BASED MATERIALS

***Faculty** of Material Science and Applied Chemistry*

***Institute** of General Chemical Engineering*

►Mg. sc. ing.
Kristaps Rubenis

►Dr. sc. ing.
Assoc. Prof.
Janis Locs

ABSTRACT

During the past few decades, thermoelectric devices have been receiving an increased attention due to the worldwide energy and environment problems. In the last few years also RTU IGCE conducts researches in the field of thermoelectric materials with the main focus on titanium dioxide based materials.

***Keywords**: thermoelectric properties, thermoelectric devices, titanium dioxide.*

INTRODUCTION

Over 65 % of the world's electrical energy used today is produced in power plants that burn fossil fuels as their source of energy. Taking into account the conversion processes, the overall efficiency of a modern fossil fuelled power plant is about 40 %, which means that around 60 % of the energy content of the fuel is lost in the form of heat. Constantly increasing prices of fossil fuels and growing environmental concerns are among the main reasons why thermoelectric materials have attracted a tremendous interest, since they can directly convert waste heat into electricity and could increase the energy efficiency of fossil fuel burning power plants and vehicles. Thermoelectric devices can be used for either power generation or cooling/heating applications. Typically, they consist of arrays of *n*- and *p*-type semiconductor materials, connected in series using metallic junctions. If a heat source is provided at the junction, it causes the carriers to flow away from the junction, creating an electrical generator. Similarly, when electric current is passed in appropriate direction through the junction, both types of charge carriers move away from the junction and convey heat away, thus cooling the junction (Fig. 1.) [1, 2].

THERMOELECTRIC PROPERTIES OF TIO_2 BASED MATERIALS

While the needs of low and mid temperature applications could be satisfied with existing thermoelectric materials, suitable high-temperature materials are still lacking. Oxide materials are recently considered to be promising thermoelectric materials for high temperature applications due to their thermal and chemical stability at high temperatures, environmental friendliness and low cost [3]. During the past decade, several researches have proven that TiO_2 is a perspective n type high temperature thermoelectric material [4, 5].

At RTU IGCE, we are trying to improve thermoelectric properties of TiO_2 based ceramic materials through different approaches — by using different shaping and sintering techniques, by optimising heat treatment conditions (sintering parame-

ters, sintering environment) as well as by making TiO_2 based composites in order to improve its thermoelectric properties. Fig. 2. shows the effect of different heat treatment conditions on thermoelectric power of cold extruded TiO_2 samples [6]. As can be seen, the values of thermoelectric power are strongly affected by thermal treatment temerature and environment. Also the shaping method can greatly affect the thermoelectric properties of TiO_2. As can be seen in Fig. 3., under the same thermal treatment conditions the values of Seebeck coefficient are higher for cold extruded (CEXed) compared to cold isostatically pressed (CIPed) samples [7]. This can be attributed to differences in microstructure of the CIPed and CEXed samples caused by different shaping technologies.

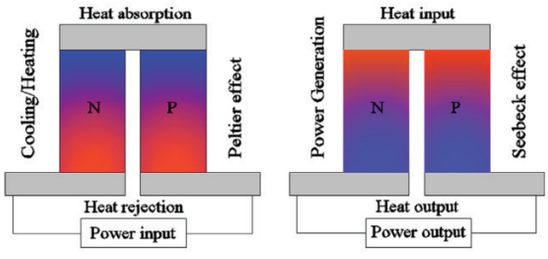

Fig. 1. *Principle configuration of single TE couple for cooling/heating and power generation*

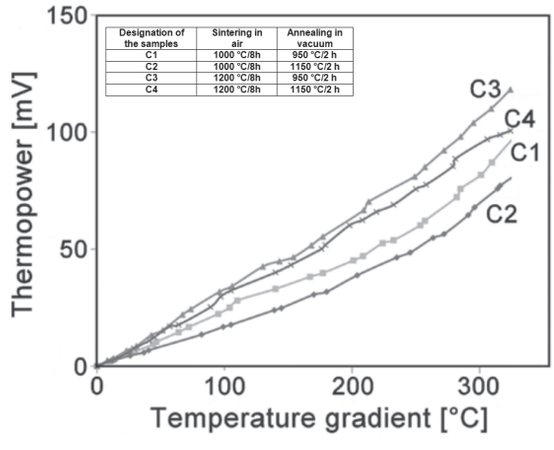

Fig. 2. *Thermopower as a function of temperature gradient for the samples*

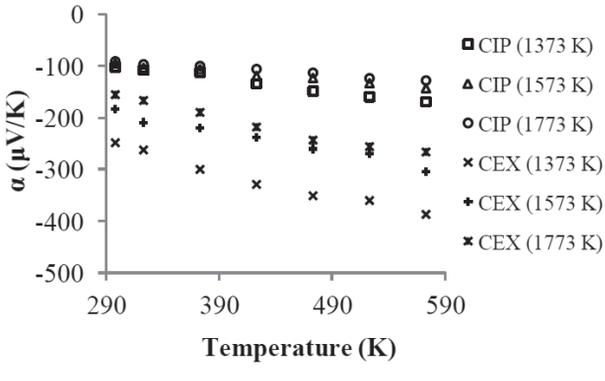

Fig. 3. *Seebeck coefficient as a function of temperature of CIPed and CEXed samples sintered at different temperatures*

CONCLUSIONS

Althoug thermoelectric properties of TiO_2 based materials are greatly improved over the last few years, for practical applications they still need to be further improved.

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KOPSAVILKUMS

Pēdējās desmitgadēs, pieaugot enerģijas un apkārtējās vides problēmām, aizvien lielāku interesi visā pasaulē rada termoelektriskie materiāli, ar kuru palīdzību siltumenerģiju tiešā veidā iespējams pārveidot elektroenerģijā un otrādi.

Pēdējos gados arī RTU VĶTI tiek veikti pētījumi termoelektrisko materiālu jomā, kuri galvenokārt vērsti, lai uzlabotu TiO_2 un SnO_2 bāzētu materiālu termoelektriskās īpašības. RTU VĶTI veikto pētījumu mērķis ir noskaidrot, kā attiecīgo materiālu termoelektriskās īpašības ietekmē materiāla iegūšanas metode, mikrostruktūra, kā arī dažādi dopējošie elementi. Līdz šim augstākā iegūto materiālu ZT (*figure of merit*) vērtība ir aptuveni 0,1.

APPLICATION OF LATVIAN CLAYS IN THE PAST AND FUTURE

***Faculty** of Material Science and Applied Chemistry*

***Institute** of General Chemical Engineering*

►Dr. sc. ing., Prof.
Līga Bērziņa-Cimdiņa

►Dr. sc. ing.
Inga Dušenkova

►Mg. sc. ing.
Jana Vecstaudža

►Mg. sc. ing.
Valentīna Stepanova

►Dr. sc. ing.
Vitālijs Lakevičs

ABSTRACT

Besides the traditional application of clays, the requirements to effective technologies for production of existing and new products from natural materials are increasing. The aim of our research is to expand the application of Latvian clays by development of novel products and technologies and by investigation of archaeological clay materials. This study gives an insight in the research of clay properties for usage in cosmetic products and sorption materials and the possible used technology and raw materials for production of archaeological ceramics.

***Keywords**: Latvian clays, cosmetic products, archaeological ceramics, sorption granules.*

INTRODUCTION

Clay is Latvian mineral wealth and their deposits are one of the largest in Northern Europe. Properties of Latvian clays are widely investigated, but the research is mostly based on application as building materials and traditional ceramics. Therefore, it is necessary to evaluate the suitability of Latvian clays for use in products with high added value. For this purpose, our research involves the investigation of clay properties for application in the development of cosmetic products and efficient sorption materials. Another direction of our research is the investigation of archaeological ceramics for further application in restoration.

Our work has been supported by the National Research Programme of Latvia 2010–2013 "Sustainable use of local resources (underground resources, wood, food and transport) — new products and technologies (NatRes)" and the research is being continued.

APPLICATION OF LATVIAN CLAYS IN COSMETIC PRODUCTS

Based on recent research about harmful influence of various chemical compounds in cosmetic products on human health and due to increasing levels of allergic reactions caused by cosmetics, the demand for cosmetics containing natural ingredients is becoming more urgent. Clays are widely used in cosmetics, health care and therapeutic products as active ingredients and additives (see Fig. 1). The most popular applications of clays are facial masks and thickeners for improvement of viscosity. Studies in recent years have shown that clays could be used as UV-filters in UV-protection creams [1].

To evaluate the application of clays in cosmetics, 125 clay-containing cosmetic products available in Latvia were investigated. Only about 3 % of them were

made in Latvia, and the most part of commercially available clay masks contain illite, which is the most abundant clay mineral in Latvia [2].

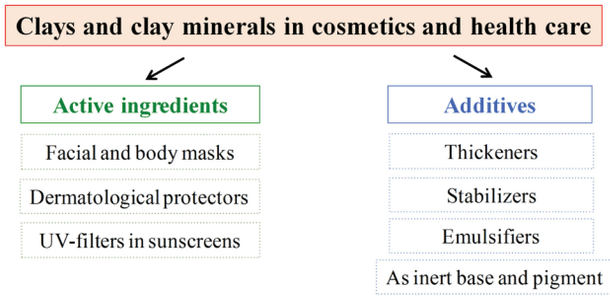

Fig. 1. *Application of clays and clay minerals in cosmetics and health care*

Application of certain clays in cosmetics depends mostly on their mineralogical composition and colour. The typical properties of clays (sorption, viscosity, plasticity), which are important in cosmetic products, are created by clay minerals. The type of a clay mineral and the presence of other minerals (calcite, dolomite, iron oxides, quartz, and feldspar) can alter these properties [1], therefore we are investigating how the purification of Latvian illite clays affects their application as facial masks, thickeners, stabilizers and UV-filters. The colour of clays found in Latvia varies from light gray to brown and red (Fig. 2), depending on the mineralogical composition.

Fig. 2. *Most common clay colours in Latvia*

Latvian clays demonstrate as good and even better adsorption properties in relation to organic compounds found on human skin than commercially available clay masks. Removal of iron oxides improves adsorption properties [3]. Addition of clay fraction (particle size <2 μm) to glycerol/water solution increases its viscosity multiple times and changes it from Newtonian to Non-newtonian solution, which is essential in cosmetic products for application on skin. The best results are shown by clays after removal of carbonates [4]. Recent research shows that clays can be used also as UV-filters in sunscreens. The best UV protection properties are shown by untreated Latvian clays with high iron oxide content [3].

SORPTION MATERIAL BASED ON LATVIAN CLAYS

Due to their sorption properties, clays can be used also as sorbents for environmental purification from organic compounds and heavy metals. The sorption properties can be changed and improved by chemical (with various organic and inorganic compounds) and thermal modification. In our research we use mostly smectite-containing clays of Triassic period (for example, Vadakste deposit) and modify them with organic compounds and thermal treatment. Thermal treatment increases sorption properties in relation to oils, water and heavy metals [5].

Our work has resulted in one patent on sorption granules for unpleasant odour elimination, being comfortable in usage for pets (see Fig. 3). They have high moisture absorption (160–170 mass %). These granules are based on Latvian clays with few per cent of carboxymethylcellulose and non-dusting agent (wood processing product) [6].

Fig. 3. *Photo of sorption granules*

INVESTIGATION OF ARCHAEOLOGICAL CERAMICS

Our institute has developed collaboration with Turaida Museum reserve within the framework of National Research Programme. We analyzed archaeological ceramics (stove tiles), which was found during excavations in Turaida. The aim of the research was to determine the provenance (used raw materials and technology) of ceramics. This knowledge gives an idea about pottery production, artistic choices, and also facilitates the conservation and restoration of objects. In last decades, research of archaeological ceramics has noticeably developed due to the progress of various research methods [7]. Ceramics provenance was analyzed with powder X-Ray diffraction, scanning electron microscope with EDS unit, high temperature microscope. Based on the results, the manufacturing technology and specifically firing regime were estimated. Archaeological stove tiles were fired at temperatures below 900 °C [8]. Composition of ancient ceramics and local clay near Turaida was similar, which suggests the use of local raw materials in preparation of ancient ceramics [8, 9].

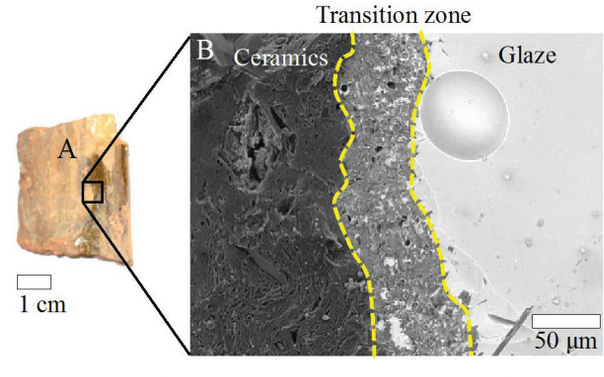

Fig. 4. *Photo of analyzed archaeological stove tile fragment (A) and micrograph (B) of the same*

CONSCLUSIONS

The results of our research show a potential of novel applications of Latvian clays have. They can be used in cosmetic products as facial masks, thickeners in semi-solid products, UV-filters in sunscreens and pigments, but additional research needs to be done. The sorption granules are environmental friendly and economical because they are produced using local resources. It can ensure a high added value for the product compared to similar imported materials. The research carried out in the field of archaeological ceramics will facilitate the work of Turaida castle restorers and conservators in near future.

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KOPSAVILKUMS

Latvija ir viena no Ziemeļeiropas valstīm, kas bagāta ar mālu resursiem. To īpašības ir plaši pētītas, bet šie pētījumi pārsvarā ir saistīti būvniecības materiālu ražošanu un tradicionālās keramikas izgatavošanu. Ir arī pētītas mālu izmantošanas iespējas kosmētisko produktu un efektīvu sorbcijas materiālu izveidē ar lielu pievienoto vērtību. Šo pētījumu rezultāti liecina, ka atkarībā no priekšapstrādes Latvijas illīta mālus var izmantot kā sejas maskas, biezinātājus un UV filtrus. Pētot mālu sorbcijas izmaiņas, kas rodas ķīmiskās un termiskās apstrādes rezultātā, ir izstrādātas efektīvas sorbcijas granulas, kuru sastāvā ir Latvijas māli un kas ir izmantojamas dzīvnieku sausajās tualetēs iekštelpās. Ir veikti arī pētījumi par Turaidas arheoloģiskās mālu keramikas sastāvu un iespējamo iegūšanas tehnoloģiju, lai atvieglotu seno krāšņu konservācijas un restaurācijas darbus.

NATURAL AND SYNTHETIC ANTIOXIDANTS FOR IMPROVEMENT OF OXIDATIVE STABILITY OF VEGETABLE OILS

***Faculty** of Material Science and Applied Chemistry*

***Institute** of Technology of Organic Chemistry*

►Mg. sc. ing., researcher
Inese Mieriņa

►Dr. chem., Prof.
Māra Jure

ABSTRACT

The impact of extracts of different plant materials on the oxidative stability of vegetable oils has been investigated. In order to predict structure-antiradical/antioxidant activity, derivatives of natural antioxidants avenanthramides, present mainly in oats, were synthesized and their activity was characterized by 1,1-diphenyl-2-picrylhidrazyl and galvinoxyl tests; few of compounds were tested as potential antioxidants for improvement of oxidative stability of biodiesel.

***Keywords**: vegetable oils, biodiesel, oxidative stability, antiradical activity, natural antioxidants, avenanthramides.*

INTRODUCTION

Vegetable oils are widely used in various fields — food, cosmetics, medicine and technique. Polyunsaturated vegetable oils (e.g., rapeseed, linseed and hempseed) are triglycerides of fatty acids, mainly oleic, linoleic and linolenic acid. Fish oil contains even more unsaturated esters of ω-3 fatty acids — eicosapentaenoic acid and docosahexaenoic acid. The polyunsaturated fatty acids are beneficial for human health: they demonstrate anti-inflammatory action, are important components of neuronal membranes and procure cardiovascular health. Insufficient intake of polyunsaturated fatty acids can cause neuropsychiatric diseases, such as major depression, bipolar disorder, schizophrenia, Alzheimer's disease, and attention deficit hyperactivity disorder.

The shortage of polyunsaturated vegetable oils is their low oxidative stability due to the presence of several *bis*-allylic and allylic positions — oxidized lipids may cause illness, e.g., they are mediators of coronary heart diseases.

Usually, the oxidative stability of oils is increased by adding synthetic phenol type antioxidants — the most typical abbreviations found on labels of cosmetic products are BHT (butylated hydroxytoluene) and BHA (butylated hydroxyanisole). The latest studies revealed drawback of these compounds, e.g., BHT promotes lung tumor in mice.

Studies devoted to vegetable oils in order to increase their oxidative stability, as well as synthetic transformations of vegetable oils and application of food processing by-products, started in RTU already more than 30 years ago under supervision of professor, *Dr. habil. chem.* E. Gudriniece. Nowadays this research continues at the Institute of Technology of Organic Chemistry under leadership of the Head of the Laboratory of Natural Products Research Professor, *Dr. chem.* M. Jure [1].

RESULTS

Our investigations were initiated by company DUO AG, which produces vegetable oils, including macerated plant oils, containing different valuable ingredients. Within the project "Implementation of innovative preparation technologies of concentrates of avenanthramides in manufacturing of biologically active products", we worked out a technology for preparation of natural antioxidant extracts and synthesized a range of analogues of natural antioxidants avenanthramides [2].

PREPARATION OF EXTRACTS OF NATURAL ANTIOXIDANTS

During the last years, our studies are devoted to the search for new sources of natural antioxidants in order to improve the oxidative stability of polyunsaturated vegetable oils and their methyl esters (biodiesel). Pomace and seeds of sea buckthorn [3], seeds, pomace and buds of black currant [4], hulls of oats [3] as well as seeds of Japanese quince [5] were used as alternative sources of antioxidants. Besides, we have studied the influence of additives of various grains — barley, oat and buckwheat — on the oxidative stability of rapeseed, hempseed and linseed oil. Two types of extracts were applied in our experiments: both organic solvents (e.g., ethanol, ethyl acetate, hexane etc.) and vegetable oils were used as extraction solvents. Several methods were used for preparation of natural antioxidant extracts:

- Extraction of plant material by (or without) stirring with vegetable oil — extracts can even be made at home;
- Cold-pressing of the mixture of plant material and oil seeds — this method is patented [7] and used at DUO AG Ltd.;
- Combined method (elaborated at our laboratory) of both previously mentioned procedures includes premaceration of the plant material in small amount of vegetable oil, followed by addition of oil seeds and cold-pressing of this mixture;
- Extraction of ground plant material with vegetable oil under ultrasonication for a short time (less than 30 min).

The oxidative stability of prepared oil extracts was determined under accelerated oxidation conditions — all samples were filled in Petri dishes and kept at 40 °C in dark. The oxidation processes were monitored by peroxide values, which were measured regularly. The peroxide value, characterizing the amount of primary oxidation products — hydroperoxides, has been determined by iodometric method. The obtained results are presented in graphs; an example of typical curves is presented in Fig. 1. Antioxidant activity is a ratio of time when peroxide value of 2 samples — with and without an additive —reaches 25 meq. O_2/kg.

The benefits of usage of above mentioned plant materials are both increased oxidative stability (the storage time of the oils could be increased up to 1.3–1.5 times; when oat grain extracts were used, oxidative stability increased even 3 times) and an effective utilization of by-products emerging from food industry. Additives of plant materials may affect not only oxidative stability, but also the flavor (in case of spice additives) and color (e.g., an additive of sea buckthorn pomace). From the safety and health viewpoint, vegetable oil extracts of plant materials are the most attractive; such extracts are ready for use.

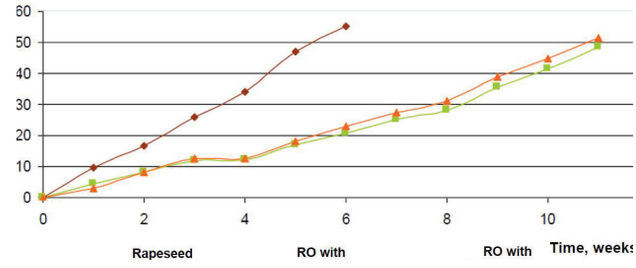

Fig. 1. *The impact of barley extracts (obtained with 70 % acetone) on the oxidative stability of rapeseed oil [12]*

SYNTHESIS OF ANALOGUES OF NATURAL ANTIOXIDANTS AVENANTHRAMIDES

Although preparation of oil extracts of plant materials is easy, the analysis of their composition is extremely complex. The prediction of structure-activity relationships and mechanisms of the action of various antioxidants in such extracts is impossible since the action of antioxidants is synergism or antagonism of a large number of different compounds. For this reason we synthesized a range of analogues of natural antioxidants. Since oat extracts demonstrated the highest antioxidant activity, we focused on analogues of unique oat antioxidants avenanthramides (basic skeleton **1**). First of all, small modifications of chemical structure were realized — replacement of substituents both in aniline and cinnamic acid moiety, hydrogenation of double bond [8] and introduction of substituent at the α-carbon in the acrylic acid fragment. Several heterocyclic scaffolds were synthesized on the basis of cinnamoyl aniline skeleton: 2-styrylbenzo-1,3-oxazinones **2**, 2-styrylquinazolinones **3**, 4-aryldihydroquinolin-2-ones **4** [9], 3-arylmethyl-4-hydroxyquinolin-2-ones **5** [10] and coumarin derivatives **6**–**8** (Fig. 2). During the studies of structure-antiradical/antioxidant activity, it was observed that monoalkyl derivatives of Meldrum`s acid **9** demonstrated the highest activity [11]. In order to predict the antiradical activity, two free radicals of different type — 1,1-diphenyl-2-picrylhydrazyl and galvinoxyl — were used. Compounds with antioxidant/antiradical activity scavenge the free radical; the quenching of the radical is observed as disappearance of color of the free radical and can be detected by a spectrophotometric method. Antiradical activity usually is characterized by two values: inhibition (%) of free radical (when ratio of radical and sample compound is 1:1) and concentration (μM) at which 50 % of the free radical is scavenged. The last value typically is calculated from curves presenting relationship between concentration and inhibition (an example of such curve is given in Fig. 3). We have established that both vanillin (or syringaldehyde) moiety and 1,3-dicarbonyl fragment are crucial for antiradical and antioxidant activity of tested compounds. Some compounds can ensure oxidative stability of biodiesel corresponding to requirements of standard LVS EN 14214.

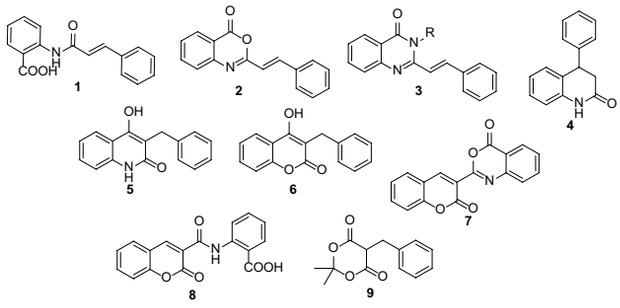

Fig. 2. *Scaffolds of avenanthramides* **1** *and their synthetic analogues*

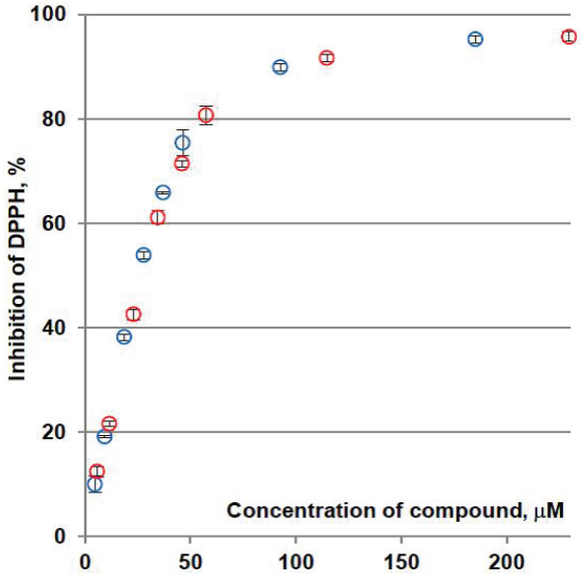

Fig. 3. *Impact of concentration on inhibition of DPPH in case of derivative of compound* **5**

CONCLUSIONS

Various analogues of avenanthramides are synthesized and new knowledge on structure-antiradical/antioxidant activity is obtained. Hulls of oats were found out a cheap source of natural antioxidants and an efficient method for extraction of natural antioxidants using ultrasound was elaborated within the project "Implementation of innovative preparation technologies of concentrates of avenanthramides in manufacturing of biologically active products", which was financed by both RTU and DUO AG Ltd.

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KOPSAVILKUMS

RTU un SIA DUO AG līdzfinansētā projekta ietvaros pētīta dažādu augu materiālu piedevu ietekme uz augu eļļu oksidatīvo stabilitāti. Noskaidrots, ka pārtikas ražošanas atkritumproduktus — auzu klijas — iespējams izmantot kā lētu antioksidantu avotu. Augu eļļu auzu kliju ekstraktu oksidatīvā stabilitāte pieaug 1,3 līdz 1,5 reizes, bet auzu graudu eļļas ekstraktu — pat 3 reizes. Lai noteiktu struktūras antiradikāļu/antioksidantu aktivitātes kopsakarības, sintezēti auzu antioksidantu avenantramīdu analogi — kanēļskābju un dihidrokanēļskābju anilīdi, kā arī heterocikli (2-stirilbenzoksazīnoni, hinazolīnoni, hinolīn-2(1*H*)-onu un kumarīna atvasinājumi); pētītas arī arilmetilmeldrumskābes — dihidrokanēļskābju anilīdu izejvielas. Savienojumu aktivitāte raksturota, izmantojot difenilpikrilhidrazila un galvinoksila testus; daži savienojumi pārbaudīti arī kā potenciāli antioksidanti, kas varētu palielināt biodīzeļa oksidatīvo stabilitāti. Pētījumu ietvaros atklāta jauna un efektīva antioksidantu klase — arilmetilmeldrumskābes.

HOLOGRAPHIC GRATING SPECTROSCOPY OF OPTICAL RECORDING MATERIALS AND THEIR PHOTOTRANSFORMATION

***Faculty** of Material Science and Applied Chemistry*

***Institute** of Technical Physics*

Scientific Research Laboratory of Material Optics

▸Dr. habil. phys.
Andris Ozols

▸Dr. phys.
Pēteris Augustovs

▸Dr. phys.
Dmitrijs Saharov

ABSTRACT

Effect of spatially periodic polarized light irradiation is experimentally studied in azobenzene compound films synthesized in the Faculty of Material Science and Applied Chemistry (group of Professor V. Kokars). Amorphous chalcogenide films and photorefractive crystals are also studied for comparison. It is shown that such irradiation can periodically modulate not only the electronic states but also the structure and shape of the materials forming various holographic gratings. Dynamic holographic gratings are efficient tools for studies of photoinduced and relaxation processes in optical recording materials. Recent experimental work in the Scientific Research Laboratory of Material Optics concerning red light surface — relief gratings, polarization hologram recording, photoinduced anisotropy and film relaxation is briefly described.

INTRODUCTION

Laser light is able to transform materials both internally and externally. This capability is based on the photoinduced processes changing the material polarization. Then photoinduced changes of absorption and refraction are related to the cubic dielectric susceptibility. These processes can lead also to the mass transfer and surface patterning by light [1]. When laser light has a spatially periodic modulation, a holographic grating is recorded, and we can speak about the holographic phototransformation of materials. It has large advantages of detecting the photoinduced processes compared to the single beam irradiation in terms of signal-to-noise ratio as well as grating period and strength variations. From practical point of view, holographic information recording and holographic optical elements (including light polarization transformers and dynamic holographic 3D TV displays) are of a high interest.

In this paper we report the results concerning the first (to our knowledge) red light surface-relief grating recording in organic materials, and namely, in stilbene azobenzene molecular glassy films [2], and the polarization holographic grating (HG) recording in amorphous chalcogenide a-As_2S_3 and a-$As_{40}S_{15}Se_{45}$ films, **8a**, **11**, **16**, **19** azobenzene compound films and in $LiTaO_3$:Fe crystals [3]. Peculiarities of light diffraction on vector gratings were studied as well. Besides, we report on the holographic studies of photoinduced anisotropy (PA) of azobenzene molecular glassy films [4] and of their dark relaxation [5].

Characteristic experimental setup (except for PA studies) is presented in Fig. 1.

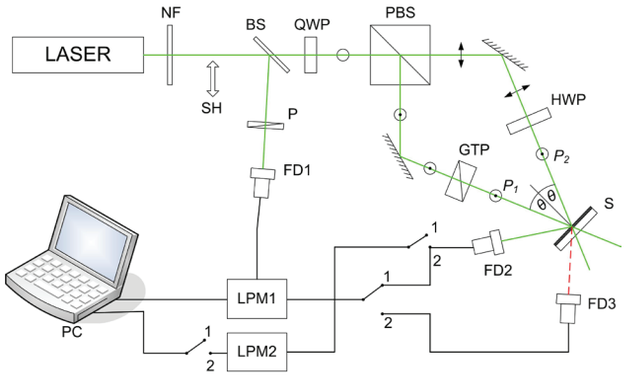

Fig. 1. *Holographic setup for recording with s-s polarizations. NF — neutral filters, SH — shutter, BS — beamsplitter, QWP — quarter-wave plate, HWP — half-wave plate, PBS — polarization beam splitter, GTP — Glan-Thompson prism, S — sample, P — polarizer, FD — photodetector, LPM — laser power meter, PC — personal computer. Position 1 — reflection SDE measurements , position 2 — simultaneous reflection and transmission SDE measurements. In the case of other recording beam polarizations the corresponding half-wave plates or quarter-wave plates in the beams P_1(or P_R) and P_2 (or P_S) before the sample were either inserted or removed.*

SURFACE-RELIEF HOLOGRAPHIC GRATINGS IN STILBENE AZOBENZENE FILMS

Holographic recording in stilbene azobenzene derivatives by He-Ne 633 nm laser light has been experimentally studied [2]. It was found that surface relief gratings (SRG) can be recorded by means of red light. Usually, shorter wavelengths are used to induce the trans-*cis* photo-isomerization in organic materials. SRG with 2 μm period and 130 nm amplitude have been recorded with 0.88 W/cm^2 light for about 20 minutes in amorphous films of the compound **8a** or 3-(4-(bis(2-(trityloxy)ethyl)amino)phenyl)-2-(4-(2-bromo-4- nitrophenyl)diazenyl)phenyl) acrylonitrile spin-coated on glass substrates (Fig. 2).

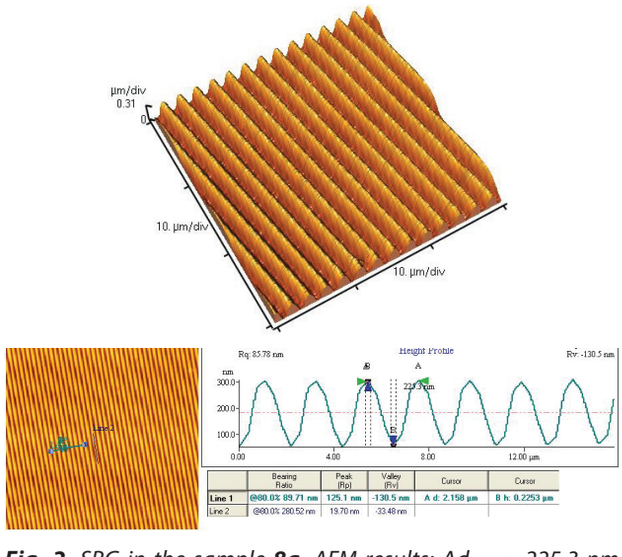

Fig. 2. *SRG in the sample **8a**. AFM results: Δd_{max} = 225.3 nm, $d1_{max} \approx$ 113 nm.*

Self-diffraction efficiency (SDE) and specific recording energy were measured. We defined SDE according to formula:

$$SDE = \frac{P_d(k=-2, l=-1)}{P_s}$$

where $P_d(k = -2, l = -1)$ is the sum of the minus-first-order diffracted power of the P_S beam and of the minus-second-order diffracted power of the P_R beam, P_S, being the incident readout light power. If $P_R = 0$, SDE is equal to diffraction efficiency (DE). Specific recording energy corresponding to a certain SDE value (usually, to SDE_{max}) was calculated according to formula $W = It / SDE$, where I is light intensity in W/cm^2, t is time in seconds.

SDE up to 17.4 % and specific recording energy down to 114 J/(cm^2%) were measured in these experiments. The recorded SRG were stable as proved by subsequent AFM measurements. The photo-induced changes in absorption spectra did not reveal noticeable signs of *trans-cis* transformations. Rather, spectrally uniform bleaching of the films took place. We conclude that a photothermally stimulated photo-destruction of chromophores is responsible for the SRG recording, at least, partially. *Trans-cis* photoisomerization is possible as well. This possibility is confirmed by a strong recording polarization dependence. Recording of stable SRG in the stilbene azobenzene derivatives is accompanied by the recording of relaxing volume-phase gratings due to the photo-orientation of chromophores by the linearly polarized recording light.

POLARIZATION HOLOGRAMS IN ORGANIC AND INORGANIC MATERIALS

Effect of recording and readout light polarization on holographic grating recording in glassy molecular azobenzene films **8a**, **11** or 4-((2-bromo-4-nitrophenyl)diazenyl)-N,N-bis(2-(triphenylsilyloxy) ethyl)benzenamine, **16** or 2-(ethyl(4-((2-nitro-4-triphenyl)diazenyl)phenyl)amino)ethyl-4-((4-bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)-3-nitro-benzoate and glassy chalcogenide a-$As_{40}S_{15}Se_{45}$ films have been experimentally studied at 633 and 532 nm with *s-s*, *p-p*, CE-1 and CE-2 circular-elliptic (differing by light electric field rotation directions) recording beam polarizations [3]. The polarization changes in the diffraction process were studied as well. Azocompounds exhibited much higher SDE and diffraction efficiency while chalcogenides were more sensitive. Their recording efficiency polarization dependences also were different and spectrally-dependent. SDE up to 45 % was achieved in **8a** with *p-p* and up to 2.8 % in a- $As_{40}S_{15}Se_{45}$ with CE-2 polarized recording beams at 633 nm. Linear *p-p* polarizations were the most efficient at 633 nm whereas CE-1 polarizations were the best at 532 nm in azocompounds. It was found that light polarization changes in the process of diffraction depended on chemical composition, wavelength and exposure time. Vector gratings with SDE up to 25 % were recorded in **8a** rotating a linear polarization by 900.

No light polarization changes were found in **8a**, **19** and chalcogenide films, and $LiTaO_3$: Fe crystals at 532 nm.

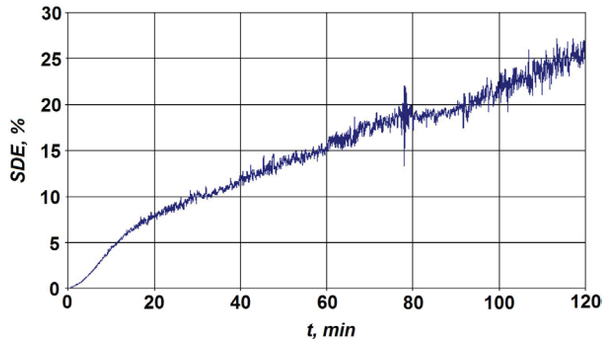

Fig. 3. *SDE exposure time dependence for sample* ***8a*** *in the case of orthogonal s-p recording beam polarizations at 633 nm.*

HOLOGRAPHIC STUDIES OF PHOTOINDUCED ANISOTROPY IN MOLECULAR GLASSY FILMS CONTAINING DIPHENYLAMINE AZOCHROMOPHORES

Photoinduced anisotropy (PA) is experimentally studied in three molecular glassy films synthesized in our Faculty and containing diphenylamine based azochromophores {4-((4-nitrophenyl)diazenyl)-N-(4-((4-nitrophenyl)diazenyl)phenyl)-N-(2-trityloxy) ethyl) benzeneamine (shortly K-D-24), 4-((2-chloro-4-tritylphenyl)diazenyl)-N-(4-((2-chloro-4-trityl-phenyl)diazenyl)phenyl)-N-(2-(trityloxy) ethyl) benzenamine (shortly K-D-25), 4,4'-(2-(trityloxy) ethylazanediyl)bis(4,1-phenylene)bis (diazene-2,1-diyl) dibenzonitrile (shortly K-D-32)} and, for comparison, in a-As_2S_3 film [4]. Holographic method enabling simultaneous measurements of *s*- and *p*-polarized diffracted light powers was applied in both transmission and reflection modes. Holographic grating recording with the period of 2 μm was made by two equally strong 532 nm *p*-polarized laser beams with total light intensity of 0.81 W/cm^2. The readout was made by 633 nm circularly polarized beam, and the *s*-and *p*-polarized components of diffracted light were separated by the polarization beam splitter prism.

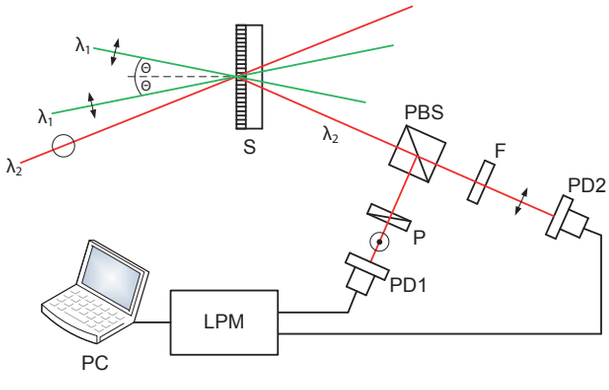

Fig. 4. *Experimental setup for transmission mode PA measurements.*

PA was characterized by diffracted power difference (DPD), $P_s - P_p$, and by anisotropy contrast $A = (\eta^s - \eta_p) / (\eta_s + \eta_p)$, η_s and η_p being the diffraction efficiencies for *s*- and *p*-polarized light.

DPD exhibited markedly different kinetic behaviour in transmission and reflection modes. There was a negative minimum in transmission mode in all samples, and a growth with oscillations up to saturation in reflection mode.

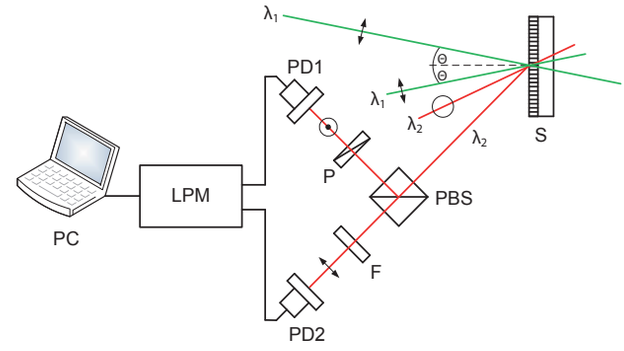

Fig. 5. *Experimental setup for reflection mode measurements.*

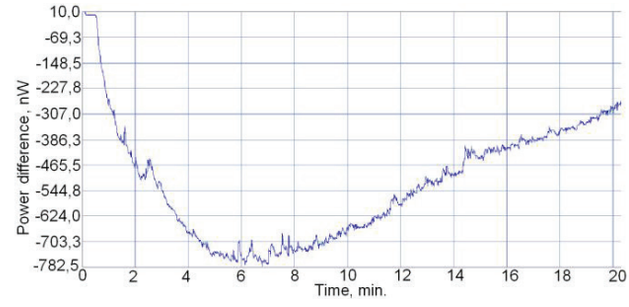

Fig. 6. *Diffracted power difference $P_s - P_p$ (nW) versus time(minutes) in the case of K-D-24 sample. Transmission mode.*

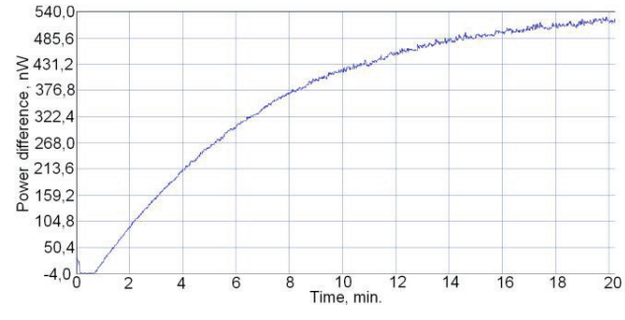

Fig. 7. *Diffracted power difference $P_s - P_p$ (nW) versus time (minutes) in the case of K-D-25 sample. Reflection mode.*

Small initial DPD maxima were specific to a-As_2S_3 film. The highest PA was found in K-D-24 film in transmission mode ($A = -0.23$) and in K-D-25 film in reflection mode ($A = 0.49$). Holographic recording efficiency and PA do not correlate. In our opinion, PA in transmission mode of molecular glasses is due to the photoinduced volume processes including *trans-cis* photoisomerization, chromophore orientation and mechanical stress modulation. In case of a-As_2S_3 film these photoinduced volume processes include photoinduced structural changes, *D*-centre orientation and, again, mechanical stress modulation. All these processes lead to a photoinduced birefringence. Surface relief grating recording and polarization-dependent reflection are responsible for diffractive anisotropy in reflection mode.

EFFECT OF HOLOGRAPHIC GRATING PERIOD ON ITS RELAXATION IN A MOLECULAR GLASSY FILM

Holographic grating (HG) relaxation has been experimentally studied in 5,5,5-triphenylpentyl 4-((4-(bis(5,5,5-triphenylpentyl)amino) phenyl) diazenyl) benzoate molecular glassy film for HG periods (Λ) of 0.50, 2.0 and 8.6 μm [5]. Transmission and reflection diffraction efficiencies (DE)

have been measured. We suppose basing on our experimental results that transmission DE characterizes mainly volume grating whereas the reflection DE characterizes mainly the surface grating. A strong effect of HG period on its relaxation is found manifesting itself differently in the volume and on the surface.

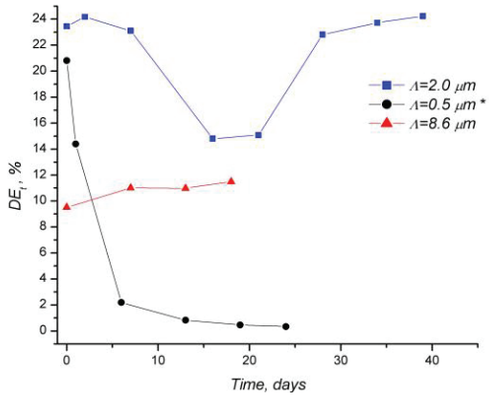

Fig. 8. *Transmission diffraction efficiency relaxation time dependences for gratings periods of 2.0 μm (blue rectangles), 8.6 μm (red triangles) and 0.5 μm (black circles). In case of 0.5 μm period 100 times larger DEt values are shown. Rectangles, triangles and circles are the experimental points. Lines are to guide the eye.*

The volume part of HG is fairly stable during 40 days if $\Lambda > 0.50$ m whereas the surface part of HG (most probably, surface relief grating) exhibits relaxational self-enhancement that is maximal at $\Lambda = 8.6$ μm.

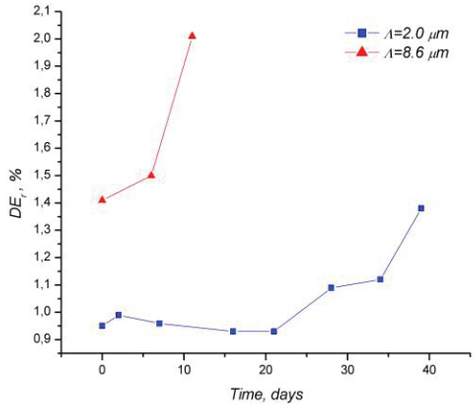

Fig. 9. *Reflection diffraction efficiency relaxation time dependences for gratings periods of 2.0 μm (blue rectangles) and 8.6 μm (red triangles). Rectangles, triangles and circles are the experimental points. Lines are to guide the eye.*

It is proposed that the thermostimulated directional mass transfer in the process of relaxation can be responsible for this relaxational self-enhancement. Weak HG recording and relatively fast HG decay take place at $\Lambda = 0.50$ μm. Therefore, effective chromophore photoorientation domain of about 0.2 μm is supposed.

CONCLUSIONS

Holographic phototransformation of organic and inorganic materials is experimentally studied. Efficient surface relief gratings are recorded in stilbene azobenzene derivatives by means of red light for the first time. It is found that red light induced *trans-cis* photoisomerization is possible.

Polarization grating recording is studied in various organic and inorganic materials, and a surprising possibility of scalar grating vector recording is elucidated. Polarization change in the process of diffraction is also observed.

Holographic method for photoinduced anisotropy of materials is proposed and applied. In case of organic molecular glassy films it is found that the photoinduced anisotropy is different within the volume and on the surface.

Holographic grating dark relaxation is also found to be different in the volume and on the surface. It also depends on the holographic grating period.

The obtained results can be applied for optimization of materials, for optical information recording and in new types of holographic optical elements.

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KOPSAVILKUMS

Materiālzinātnes un lietišķās ķīmijas fakultātē profesora V. Kokara grupā veikti eksperimentāli pētījumi, kuros noskaidrota telpiski periodiskas polarizētas gaismas starojuma iedarbība uz sintezētām azosavienojumu kārtiņām. Salīdzinājumam ir pētītas arī amorfo halkogenīdu kārtiņas un fotorefraktīvie kristāli. Ir parādīts, ka šāds starojums var modulēt ne tikai elektronu stāvokļus, bet arī materiālu struktūru un formu, veidojot holografiskos režģus. Dinamiskie holografiskie režģi ir efektīvi rīki, lai pētītu fotoinducētos un relaksācijas procesus optiskā ieraksta materiālos. Rakstā ir īsi apskatīti Materiālu optikas zinātniski pētnieciskajā laboratorijā veiktie eksperimenti, kuros pētīti ar sarkano gaismu ierakstītie virsmas reljefa režģi, polarizācijas hologrammas, fotoinducētā anizotropija un kārtiņu relaksācija.

SEMICONDUCTOR NANOSTRUCTURE FORMATION BY LASER RADIATION

***Faculty** of Material Science and Applied Chemistry*

***Institute** of Technical Physics*

Scientific Research Laboratory of Semiconductor Physics

►Dr. habil. phys., Prof.
Artūrs Medvids

►Dr. phys.
Pāvels Onufrijevs

►Dr. phys., Doc.
Aleksandrs Mičko

ABSTRACT

A new laser method is elaborated for the formation of nanocones on the surface of elementary semiconductors Si, Ge and semiconductor solid solutions — $Si_{1-x}Ge_x$ / Si and $Cd_{1-x}Zn_xTe$. Strong changes in optical, mechanical and electrical properties of the semiconductors after irradiation by Nd:YAG laser are explained by the Quantum Confinement Effect (QCE) in nanocones with tip radius equal to or smaller than Bohr's radius of electron, hole or exciton. The phenomena of "Blue shift" of photoluminescence spectra and "red shift" of the phonon LO line in the Raman spectrum are explained by exciton and phonon QCE in nanocones, respectively.

***Keywords**: laser, nanostructure, nanocone, quantum confinement effect, graded band gap structure.*

INTRODUCTION

Semiconductor nanostructures, such as: quantum wells — 2D (Fowler *et al.*, 1966), quantum wires (QWs) — 1D (Xia *et al.*, 2003) and quantum dots (QDs) — 0D (Alivisatos, 1996), have attracted an extensive interest due to their unique optical, electrical and mechanical properties and their potential applications in many fields. Such attention to nanostructures is due to the presence of quantization of electrons and quasi particles confined in nanocrystals — the so called Quantum Confinement Effect (QCE) (Furukawa and Miyasato, 1988). The QCE takes place in a semiconductor or metal when at least one dimension of the crystal is less than or equal to Bohr's radius of electron, hole or exciton. Nowadays, there are some well developed methods for the formation of nanostructures (NSs), such as, molecular beam epitaxy (MBE), ion implantation, and laser ablation. Methods mentioned above require subsequent thermal annealing of the structures in a furnace. Nanocrystal growth is time consuming and requires high vacuum or inert gas environment. As a result, nanocrystals grow in uncontrollable manner, broad size and spatial distribution: so called self-assembly (Zhao *et al.*, 2006). Therefore, one of important tasks in nano-electronics and optoelectronics is to elaborate new methods for NSs formation in semiconductors with controlled parameters.

A new laser method designed for nanocone formation on the surface of semiconductors is reported. A two-stage model of the nanocones formation is proposed.

EXPERIMENTS AND DISCUSSIONS

Radiation from a pulsed Nd:YAG laser for Ge single crystals and Si_xGe_{1-x}/Si solid solution was used with the following parameters: pulse duration τ = 15 ns, wavelength λ = 1064 nm, pulse rate 12.5 Hz, power P = 1.0 MW and energy W = 30.0 mJ. For Si single crystals with SiO_2 natural cover layer, second harmonics with τ = 10 ns and λ = 532 nm were used. The SiO_2 cover layer in experiments with CdZnTe for preventing evaporation of material was used. Usually, laser beams were directed to the irradiated surface of the sample. Ge (001) *i*-type single crystal samples with sizes $1.0 \times 0.5 \times 0.5$ cm^3 and resistivity $\rho = 45\Omega$ cm were used in experiments. The samples were polished mechanically and etched in HNO_3:HF:CH_3COOH (5:3:3) solution to ensure the minimum surface recombination velocity S_{min} = 100 cm/s on all surfaces. The laser beam spot of 3 mm diameter was scanned over the sample surface by a two-coordinate manipulator in 20 µm steps. The surface topography was studied by means of atomic force microscope (AFM). Optical properties of the irradiated and non-irradiated samples were studied using the photoluminescence (PL) and back scattering Raman methods. For PL, the 442 nm line of a He-Cd laser was used, and for micro-Raman back scattering — Ar + laser with λ = 514.5 nm.

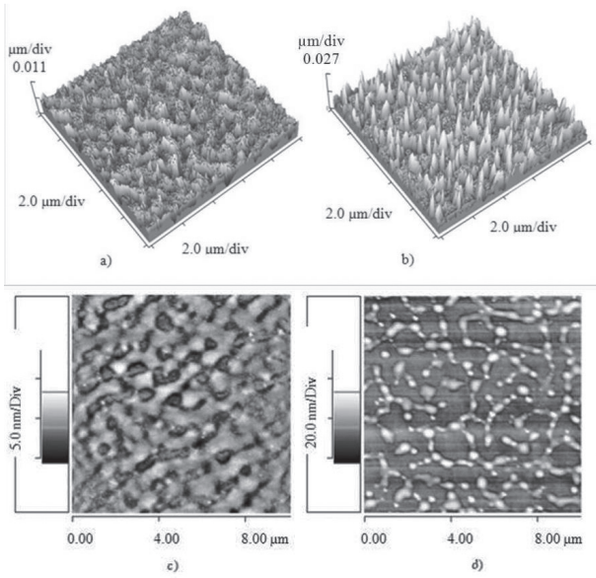

Fig. 1. *Three-dimensional AFM images of $Si_{0.70}Ge_{0.30}$/Si surfaces irradiated by Nd:YAG laser at intensity (a) 7 MW/cm^2 and (b) 20 MW/cm^2 and two-dimensional surface morphology of the same spots of structure at intensities: (c) 7.0 MW/cm^2 and (d) 20.0 MW/cm^2*

200 nm thick crystalline $Si_{1-x}Ge_x$ alloy layer was grown on 150 µm thick Si(100) wafers by MBE on top of Si. Alloys containing 30 % and 40 % Ge were used in the experiments. The surface of SiGe/Si structure was irradiated by basic frequency of the Nd:YAG laser. The three-dimensional surface topography of $Si_{1-x}Ge_x$/Si hetero-epitaxial structure recorded by AFM measurements after irradiation by the Nd:YAG laser at intensities 7.0 MW/cm^2 (a) and 20.0 MW/cm^2 (b) is shown in Fig. 1. Figure 1(a) shows the nano**cones** with 11 nm average height formed by laser radiation at intensity 7.0 MW/cm^2. Similar nano**cones** with 27 nm average height shown in Figure 1(b) have been obtained by irradiation with intensity 20 MW/cm^2. Due to higher irradiation intensity, they are higher and more compact in diameter.

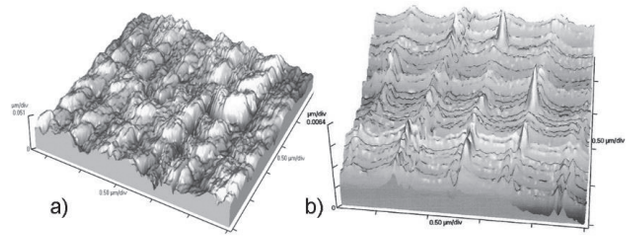

Fig. 2. *AFM 3D images of: (a) SiO_2 surface after irradiation of SiO_2/Si structure by Nd:YAG laser at I = 2.0 MW/cm^2 and (b) Si surface after subsequent removal of SiO_2 by HF acid*

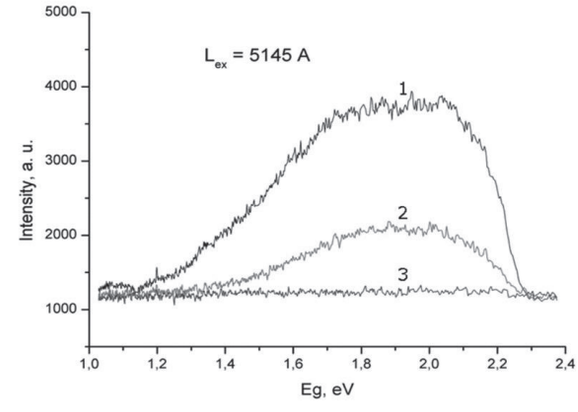

Fig. 3. *Photoluminescence spectra of the SiO_2/Si structure irradiated by laser at intensity 2.0 MW/cm^2 (2. and 3. curves), after removal of SiO_2 layer by chemical etching in HF acid (3. curve). 1. curve correspond to PL of non-irradiated surface*

Photoluminescence of SiO_2/Si structure (Fig. 2(a)) in the visible range of spectrum with maximum at 2.05 eV obtained after irradiation by laser at intensity I = 2.0 MW/cm^2, as shown in figure 3, is unusual. The maximum band in PL spectrum is usually situated at 1.0 eV and the intensity of PL is very low due to indirect band structure of Si crystals. PL of this structure after removal of SiO_2 layer (Fig. 2(b)) by wet etching in HF is similar and is obtained in the same region of spectrum, having the same positions of maximums. It means that PL is not associated with local Si-O vibration at the Si-SiO_2 interface (Fernandez *et al.*, 2002). Therefore, we explain our results by Quantum confinement effect in nano**cones**. Decrease of PL intensity can be explained by the increase in reflection index of the structure after removal of SiO_2 layer. We can see that the visible PL spectrum of SiO_2/Si structure is wide and asymmetric, with gradual decrease of intensity in IR range of spectra. It is unique to PL spectrum typical for the graded band gap structure. These results demonstrate a dramatic rise of PL intensity with a much higher band gap than with indirect Si. A schematic image of a nano**cone** with a gradual decrease in diameter from p-Si substrate to the top is shown in Figure 7. An increase in photon energy from substrate to the top of the Si single crystal at photoluminescence of nano**cone** takes place due to Quantum confinement effect in nanowire, according to formula (Li and Lin-Wang, 2004).

$$\Delta E_g = \frac{2\hbar^2\zeta^2}{md^2}, \quad (1)$$

where $1/(m^*) = 1/(m_e^*) + 1/(m_h^*)$, ($m_e^*$ and m_h^* are electron and hole effective masses, respectively) and ***d*** is the diameter. For QWs, $\zeta = 2.4048$. In our case, the diameter of nano**cones**/nanowires is a function of height ***d(z)***, therefore, it is a graded band gap semiconductor. Our calculation of Si band gap as a function of nanowires ***d*** from PL spectrum using formula (1) from paper (Li and Lin-Wang, 2004) is shown in Figure 4. We can see that the dependence is non-linear and that the band gap is a function of diameter and is decreasing. In our case, the maximum band gap is 2.05 eV, which corresponds to the minimal diameter 2.3 nm on the top of nano**cones** /nanowires.

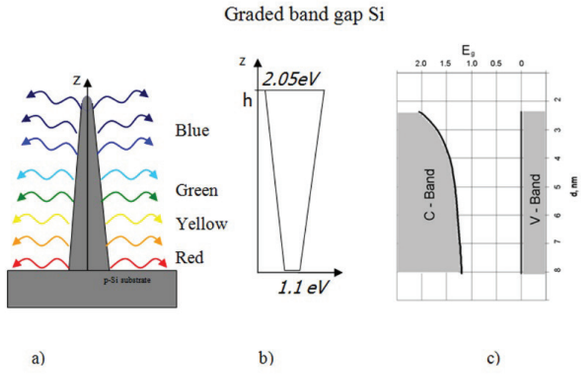

Fig. 4. *Schematic image of a nanocone with a gradually decreasing diameter from p-Si substrate to the top, formed by laser radiation — (a) and (b). Calculated band gap structure of Si as a function of nanowires diameter using formula (2) from Li and Wang (2004) — (c)*

We have found a unique method of forming a 1D graded band gap semiconductor structure. The graded change of the band gap is due to the Quantum confinement effect.

Nanocone formation on a surface of $Cd_xZn_{1-x}Te$ solid solution with $x = 0.1$ after irradiation by strongly absorbed Nd:YAG laser radiation with intensity $I = 12.0$ MW/cm^2 was observed using AFM, as shown in Figure 5. Studying the nanocones optical properties, a new exciton band at energy up to 1.87 eV in PL spectrum was observed for the first time. At the same time, a shift of A^0X and D^0X exciton lines by 3.1 and 2.5 meV, correspondingly, towards the higher energy of quantum, that is the so-called "blue shift", was observed, as shown in Figure 6. Appearance of a new PL band is explained by the Exciton quantum confinement (EQC) effect in nanocones and the "blue shift" of the exciton bands by mechanical compressive stress of the sample top layer formed on the irradiated surface of the samples. This process is described in the following way: irradiation of $Cd_{1-x}Zn_xTe$ solid solution by laser leads to the drift of Cd atoms towards the irradiated surface, and of Zn atoms — in the bulk of the semiconductor due to a high gradient of temperature, the so-called Thermogradient effect (TGE) (Medvid', 2002). As a result, formation of $CdTe/Cd_{1-x1}Zn_{x1}Te$ hetero-structure, where $x_1 > x$, takes place due to replacement of Zn atoms by Cd atoms at the irradiated surface. At the same time, the opposite process takes place under the top layer, in the buried layer of the semiconductor — Zn atoms replace Cd atoms.

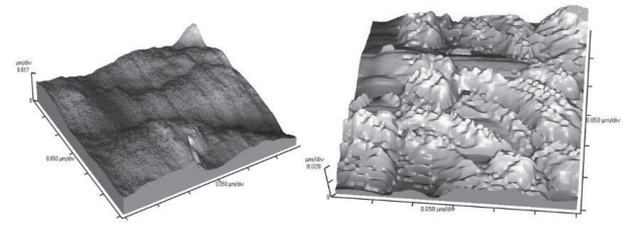

Fig. 5. *Atomic force microscope 3D images of $Cd_{1-x}Zn_xTe$ (x = 0.1) surfaces: (a) before irradiation and (b) after irradiation by laser at intensity 12 MW/cm^2*

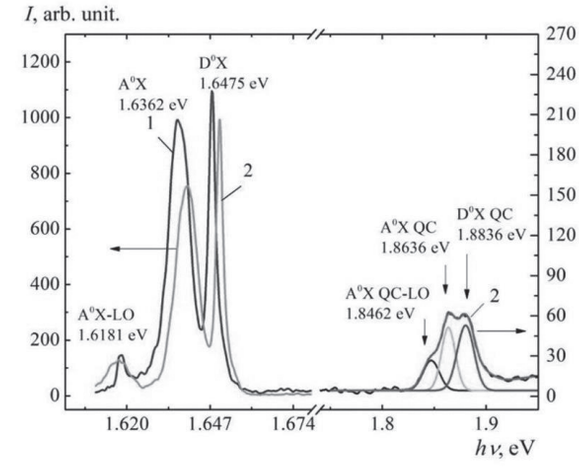

Fig. 6. *Photoluminescence spectra of $Cd_{1-x}Zn_xTe$ (x = 0.1) measured at temperature 5 K: curve 1 before and curve 2 after irradiation by laser at I = 12.0 MW/cm^2*

Relaxation of mechanical compressive stress in CdTe layer is manifested as a self-assembly of nanocones on the irradiated surface of the structure like Stransky-Krastanov's mode, and simultaneous appearance of a new exciton band at 1.872 eV in PL spectrum at high intensity of LR takes place. Deconvolution of this band shows that it consists of three lines which look like A^0X, D^0X and A^0X–LO lines (distance between the lines and intensities ratio are the same) in the non-irradiated PL spectrum of the semiconductor. Therefore, we associate the appearance of both the new band in PL spectrum and the nanocones formation on the irradiated surface of the semiconductor with EQC in nanocones and denote them as A^0XQC and D^0XQC lines.

We propose the following method of nanocone formation on the irradiated surface of Ge_xSi_{1-x} and $Cd_xZn_{1-x}Te$ solid solutions. The mechanism is characterized by two stages — Laser Redistribution of Atoms (LRA) and Selective Laser Annealing (SLA) (Medvid' *et al.,* 1997) and (Yonenaga *et al.,* 2005). The first stage of the process, LRA, involves the formation of hetero-structures, such as Ge/Si due to the separation of Ge and Si atoms in Ge_xSi_{1-x} sample and CdTe / $Cd_{x1}Zn_{1-x1}Te$ in $Cd_{x0}Zn_{1-xo}Te$ ($x_1 > x_0$) solid solutions due to TGE. The second stage, SLA, involves the formation of nanocones on the irradiated surface of a semiconductor. Heating of the structure, followed by mechanical plastic deformation of the strained top layer, leads to the formation of nanocones. The mechanical plastic deformation is caused by relaxation of mechanical compressive stress arising between these layers due to mismatch of crystal lattices and selective laser heating of the top layer.

The formed quantum cones can be applied for design of third generation solar cells, Si white light emitting diode, photodetector with selective or "bolometer" type spectral sensitivity and Si tip for field electron emitter with low work function.

CONCLUSIONS

1. The method of cone-like nanostructure formation on the surface of single crystalline semiconductors Ge, Si and SiGe CdZnTe by powerful Nd:YAG laser radiation has been elaborated.

2. For the first time a method has been elaborated for the formation of 1D graded band gap semiconductor structures. Graded change of band gap arises due to the QCE in nanocones.

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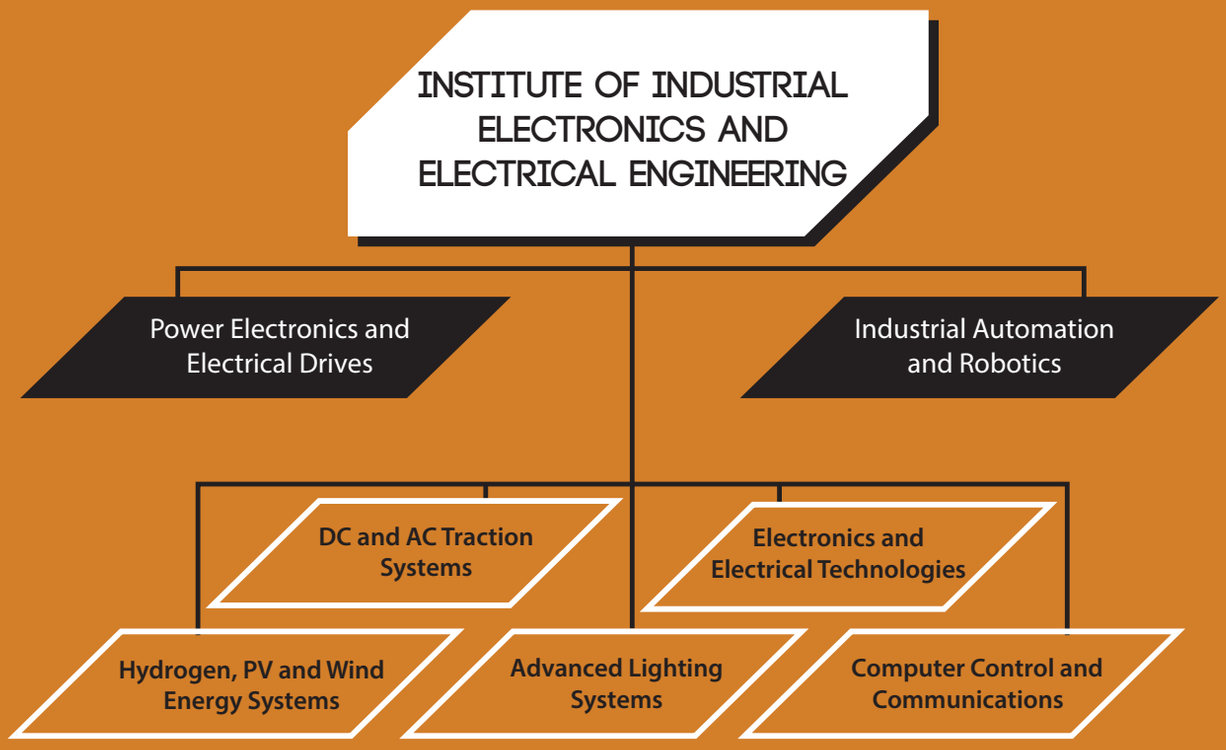
KOPSAVILKUMS

Apstarojot ar lāzera starojumu tīru pusvadītāju silīcija (Si) un germānija (Ge), kā arī pusvadītāju cieto šķīdumu $Si_{1-x}Ge_x$/Si and $Cd_{1-x}Zn_xTe$ virsmu, tika izstrādāta jauna metode nanokonusu veidošanai uz pusvadītāju virsmas. Pēc apstarošanas ar Nd:YAG lāzeru būtiski izmainās pusvadītāju optiskās, mehāniskās un elektriskās īpašības. Šo īpašību izmaiņas tiek skaidrotas ar Kvantu Ierobežojuma Efektu (KIE) nanokonusos, ja konusa virsotnes rādiuss ir vienāds vai mazāks par elektrona, cauruma vai eksitona Bora rādiusu. Zilā nobīde fotoluminiscenses spektros un sarkanā nobīde fononu LO līnijai *Raman* spektrā tiek skaidrota ar eksitonu un fononu KIE nanokonusos.


INSTITUTE OF INDUSTRIAL ELECTRONICS AND ELECTRICAL ENGINEERING
Power Electronics and Electrical Drives
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DC and AC Traction Systems
Electronics and Electrical Technologies
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Advanced Lighting Systems
Computer Control and Communications

INTELLIGENT LED STREET LIGHTING SYSTEM – LITES PROJECT AT RIGA TECHNICAL UNIVERSITY

***Faculty** of Power and Electrical Engineering*

***Institute** of Industrial Electronics and Electrical Engineering*

►M. sc. ing.
Ansis Avotins

►Dr. sc. ing.
Peteris Apse-Apsitis

►M. sc. ing.
Maris Kunickis

►Dr. habil. sc. ing., Prof.
Leonids Ribickis

ABSTRACT

Energy saving plays a significant role in nowadays European political and economical decisions. Street lighting system is a vital necessity for each city, but it consumes a lot of electrical energy to produce light, therefore energy saving is a topical problem in this case. Article gives an overview of European Framework project called LITES [1, 2] main results, describing the intelligent street LED lighting system technology architecture developed and focusing on energy saving real life experimental results at Riga Pilot Site.

***Keywords**: lighting, lighting control, Smart Grids, LED lamps.*

INTRODUCTION

The street lighting system is a necessity in order to have a safe city traffic and increase the comfort level for citizens, and in most cases the lighting systems tend to be as wide as the city street layout itself, therefore it has a lot of luminaries, consuming a significant amount of electrical energy.

The current lighting networks and systems that are designed for High Pressure Sodium (HPS) vapour source luminaries typically have centralized control systems [3], mainly used only for powering ON or OFF the electrical cabinets (or substations) where several sub-cabinets and streets with luminaries are connected. In this case, the lighting network control signal is transferred by means of radio or GPRS communication method. The system has a calendar graphic/table, where ON/OFF time is specified for each day, throughout the year, then the control command can be sent automatically or by system operator (personnel). For smaller cities and areas, in order to obtain more savings, it is common to use also delay timers, especially for low traffic streets, in this case the light comes ON later than in the rest of city, at the same time it also smoothes out the load pikes on the electrical grid.

Next step in such system evolvement is to develop new LED drivers [5], regulation techniques [4] and add communication (radio or power line) facilities [3], in order to obtain hourly consumption of each lighting pole and by adding movement detection sensors on each pole, to obtain maximum energy savings as light won't be lit if there is no traffic participant on the street. Therefore several international partners from universities and industry launched a European Framework project called LITES, and this article shows some overview on the results.

LITES PROJECT DESCRIPTION

LITES project started at the end of 2009, with main objective to demonstrate in real life experimentation that intelligent street lighting using solid-state lights LED drastically reduces energy consumption, while the lighting service delivered is compliant with road classes CE2–CE5, *S*- and *A*- according to the standard of EN13201. Fulfilling it means that LITES technology can be installed on a secondary street, commercial access, allotment, pedestrian way, cycle track, and it is compliant with all electric standards for luminaries general requirements and tests as well. The project was ambitious even at that time, therefore the project team faced many difficulties, but after five years it was eventually successful. The LITES technology is being tested at 3 different pilot sites in Riga RTU Campus (Latvia), Bordeaux (France) and Aveiro (Portugal), more info available at LITES project web-page.

DEVELOPED SYSTEM

The LITES project has developed a street lighting solution that provides a significant energy saving potential up to 70 %. The LITES technology is an intelligent public street lighting service using solid-state LED luminaries with embedded intelligence. The core element of the solution is the dimming of the lamp depending on the environment parameters; a set of embedded sensors measures the ambient light, temperature, current, and detects motion. Output data of sensors is then processed by the embedded intelligence allowing optimum regulation of light (intensity) levels.

The embedded intelligent control of the light dimming ensures a significant drop of energy consumption while fully respecting the European standards of security ruling the target category of public places.

To make lighting system more robust and thus more attractive to the lighting market, it is wise to make the LED luminary power supply with integrated control node, as shown in system architecture (Fig. 1).

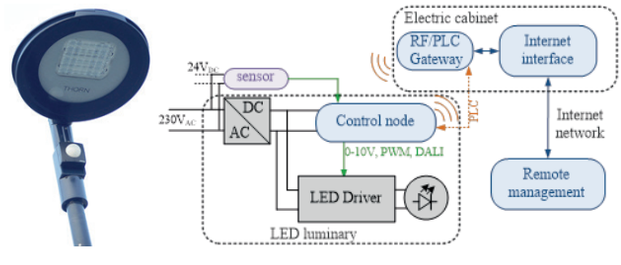

Fig. 1. *Developed LITES luminary (right) and LITES system architecture (left)*

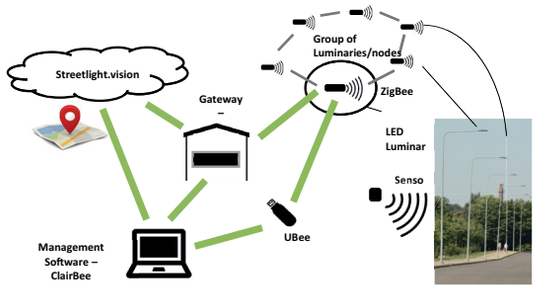

Fig. 2. *LITES technology communication architecture*

The LITES technology (see Fig. 2) consists of three main blocks: 1 — Luminary, sensor and communication node; 2 — Gateway and Network infrastructure, 3 — Local management tool and online management tool Streetlight vision. UBee is a ZigBee network communicator to enable configuration of stand-alone parameters of each LITES luminary, dedicated for maintenance engineers. The gateway enables the network management and data transfer to WEB server, where both energy and sensor data can be analyzed.

RTU PILOT SITE AND ITS ENERGY SAVING RESULTS

The RTU campus is a pilot site situated furthest to the north, therefore weather conditions and daylight hours differ from other LITES project Pilot Sites. The maximum temperature variations between winter and summer can reach up to 60 degrees Celsius (from –30 °C in winter to +30 °C in summer). The climate of Riga is humid continental and proximity of the sea causes frequent autumn rains and fogs. In Riga Pilot Site, 29 LITES LED luminaries are installed, of which 10 are located on Zunda Krastmala Street (mainly car traffic, see Fig. 3), 15 are located inside RTU Campus with mainly pedestrian traffic, 4 are located at Azenes Street for different movement detection sensor testing.

Fig. 3. *LITES luminaries on Zunda Krastmala in Riga (R2)*

All 10 pcs of R2 street profile poles (95 W luminaries) are equipped with ABB energy counter to compare the energy readings between standard counters and the LITES system. Additional 5 pcs of ABB counters are installed in existing poles with HPS lamps to obtain data and be able to compare the average efficiency in this case. The total installed power for Riga Pilot Site is 2,215 W.

Also knowing the exact times when Riga City is turning ON/OFF the lighting system, it is possible to analytically calculate energy savings that are achieved only by retrofitting, replace old High Pressure Sodium (HPS) luminary with LITES LED luminary without sensors and communication system. In this case energy savings reach up to 42%.

Also for further calculations and LITES reading justification and comparison, we should calculate the Riga Pilot Site lighting system "minimum", where luminaries are at 15 % power level, and "maximum", where luminaries are at 100 % power level, consumption values, as we do not know the traffic intensity, and thus how many times the sensor will trigger the luminary to max light (power) output. Fig. 4. represents overall Riga Pilot Site energy consumption for last months, the values are obtained via gateway and management software. In order to compare the total LITES technology (incl. sensors and communication) consumption against total HPS luminaries, 10 pcs of 157 W and 15 pcs of 117 W HPS luminaries (real measured wattage for HPS) are used for such comparison, which are multiplied by lighting hours — same as for LED luminaries. In this way we obtain

results shown in Fig. 4, with LITES technology energy savings up to 72–73 %.

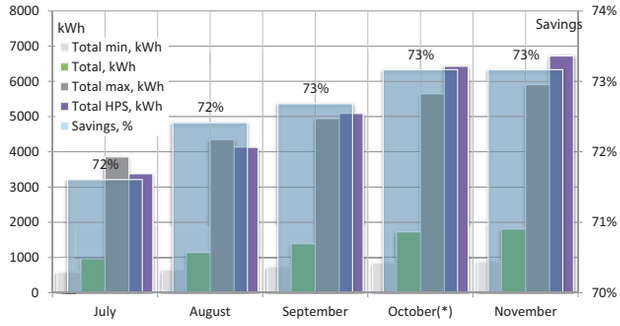

Fig. 4. *Energy consumption at Riga Pilot Site*

CONCLUSIONS

The measurements show that using LITES technology it is possible to get additional 30 % of energy savings, thus reaching 73 % in total. The research also shows that more energy savings are obtained in pedestrian zones, and little less in street areas. More energy savings are possible if system initial (stand-alone) parameter (like min and max values) configuration is fine-tuned for specific street and its traffic intensity.

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KOPSAVILKUMS

Mūsdienās Eiropas politikā un ekonomikā aktuāla tēma ir enerģijas taupīšana, kas atspoguļojas Eiropas finanšu instrumentu programmās. Katras pilsētas neatņemama sastāvdaļa ir ielu apgaismojuma sistēma, kas patērē ļoti daudz elektroenerģijas, tādēļ enerģijas taupīšana šajā gadījumā ir svarīgs uzdevums. Raksts sniedz ieskatu Eiropas Ietvarprogrammas projekta LITES galvenajos rezultātos, aprakstot izstrādātās inteliģentās ielu LED apgaismojuma sistēmas tehnoloģijas arhitektūru, kā arī parādot enerģijas ietaupījuma rezultātus, kas iegūti reālos praktiskos mērījumos, kuri veikti testēšanas poligonā Rīgā.

RESEARCH AND DEMONSTRATION OF NEW DC POWER SUPPLY CONCEPTS FOR EU FACTORIES OF FUTURE AT RTU

***Faculty** of Power and Electrical Engineering*

***Institute** of Industrial Electronics and Electrical Engineering*

►M. sc.
Armands Senfelds

►M. sc. ing.
Ansis Avotins

►Dr. habil. sc. ing., Prof.
Leonids Ribickis

***Faculty** of Power and Electrical Engineering*

DAIMLER AG

►Dr. Sc. ing.
Davis Meike

ABSTRACT

As a part of EU FP7 research project AREUS — Automation and Robotics for European Sustainable Manufacturing, research and demonstration activities in the field of DC electrical power supply for industrial equipment at Riga Technical University, Institute of Industrial electronics and Electrical Engineering (IEEI) are realised.

New concepts leading to the increase in energy efficiency and system optimisation by transition from AC to DC power supply will be verified, which will enable to design the factories of future, aiming at highly automated production processes with incorporation of industrial robots.

***Keywords**: DC microgrid, industrial robotics, energy efficiency, smart grid.*

INTRODUCTION

Common research project under title AREUS — Automation and Robotics for European Sustainable Manufacturing — within EU 7th Framework Programme call for Factories of Future aims to future challenges in the field of energy efficiency within future manufacturing. Within the period of 3 years, a consortium of 10 partner organizations from six EU partner countries (Italy, Germany, Sweden, Finland, Denmark and Latvia) will develop smart and energy efficient solutions for industrial robotics. [1] The consortium includes technology providers/developers, systems integrators/robotic plant builders, engineering services (design, simulation, optimization, LCA) providers and final users.

In the building of RTU Institute of Industrial Electronics and Electrical Engineering (IEEI), Riga, new research facility representing Industrial robot test bench will demonstrate new functions of electrical energy exchange. The core idea is utilization of direct current (DC) energy transfer link, enabling smart utilisation of energy storage technologies and integration of renewable energy sources directly close to final energy consumers within manufacturing processes.

Regarding automotive manufacturing as one of most automated industries with a high degree of industrial robot application, several aspects of energy efficiency increase have been examined previously in collaboration with RTU Institute of Industrial Electronics and major automotive manufacturer Daimler AG, resulting in doctoral thesis [2] and experimental field testing within real production environment at assembly plant in Sindelfingen, Germany [3]. Future goals and initiatives set by EU in the increase of energy efficiency and reduction of emissions are strong driving forces to support research and optimization activities looking for opportunities in energy saving and smart utilisation in various industries.

The goal of reducing by 20 % the greenhouse gas emission compared to 1990, and 20 % improvement in EU energy efficiency according to EU2020 policy [4], present both challenges and opportunities to increase the competitiveness of industrial manufacturing systems. On the other hand, willingness to incorporate more and more renewable resources in existing power systems demands new concepts of power conditioning and distribution. Major future power system development policy, such as "Energiewende" [5] in Germany, would require to modify also the existing manufacturing systems in order to utilize new opportunities presented by ever increasing renewable energy sources.

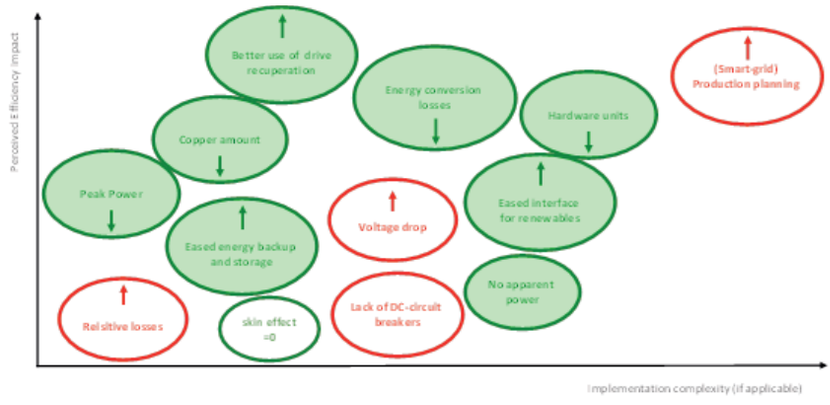

Fig. 1. *Overview of perspective impact of energy efficiency*

Fig. 2. *Visualisation of RTU AREUS Demo cell*

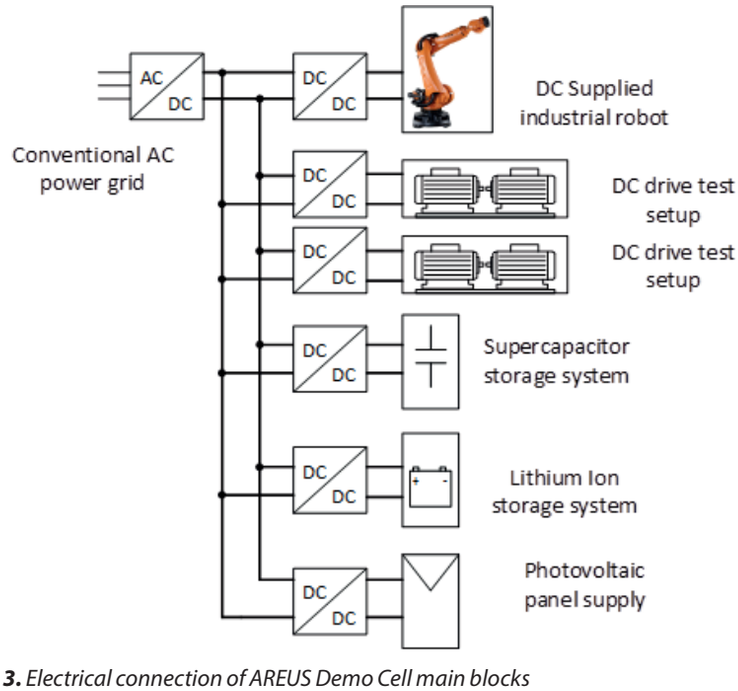

Fig. 3. *Electrical connection of AREUS Demo Cell main blocks*

Also the vision of future manufacturing represented in German national initiative — *Industrie* 4.0 [6], promoting an individualised, adaptive and fast production based on digital communication technologies, would present new functionalities also from energy utilisation perspective.

Transition from AC based supply to DC based supply provides several optimization advantages. Most challenges of DC energy supply are in the field of electrical safety and standardisation since such system components are not widely produced, applications vary significantly and are often one of the kind. An overview of perspective impact of energy efficiency in relation to implementation effort are presented in the following Fig. 1.

INDUSTRIAL DC MICROGRID DEMONSTRATION LABORATORY

Conventional AC power network within Industrial areas often faces several stages of energy conversion before supplied to load. AREUS project approach is introducing the concept of DC based energy distribution within a certain production area.

In RTU Institute of Industrial Electronics and Electrical Technologies, new 600 V DC voltage based supply system is being built to serve as the basis for demonstration of intelligent energy management and integration of renewable and energy storage functionalities. Demonstration of industrial robot application together with a set of 2 laboratory electrical drive setups presented in [7] will provide an opportunity to emulate the dynamic power flow within DC system and interact with energy storage and photovoltaic supply systems. Schematic representation of intended RTU AREUS Demo cell (see Fig. 2.) electrical power components is represented in Fig. 3.

Such structure will allow to eliminate the necessity of many AC to DC power conversion stages by introduction of a single AC/DC power conversion that would also enable the transfer of electrical energy back to AC power grid, if necessary. Energy storage would be possible by two different storage technologies — high power and fast supercapacitor based storage unit and electrochemical storage by means of lithium ion battery pack.

Additionally, 11 photovoltaic panels of nominal power 300 watts would serve as 3.3 kW nominal solar power plant located on the roof of the faculty building.

EXPERIMENTAL MODELLING OF DC SYSTEM OPERATION

Energy consumption modelling of industrial robots has been covered within AREUS project. Detailed industrial robot modelling examples have been presented in [8]. Scope of RTU research lab covers the interaction of different DC electrical subsystems, including industrial robot. Computer simulation has been carried out in order to examine the operational behaviour of DC system under conditions when DC industrial robot and a set of 2 electrical drives operate with acceleration and deceleration processes resulting in bidirectional power flow. Fig. 4. represents the current variation within single load units being drives or robot from *I*1 to *I*3 and total *Itotal* current that would be necessary for 600 V DC system supply.

It was necessary to perform the analysis of such current behaviour with respect to time. The following figure represents the highest root-mean-square (RMS) current value within various time periods. Also data on behaviour of electrical fuses according to conducted current and time has been provided by fuse manufacturers.

Analysis of modelled current profiles allows to decide what would be the appropriate fuse rating for the desired operation. In particular case, fuses with rating of 4 amperes provide a close match with single load currents that are expected to arise for supply of DC electrical drive setups or DC industrial robot.

POWER SMOOTHING CONCEPT

Utilisation of energy storage functionality in combination with dynamic loads would enable power smoothing operation. Such approach would allow more stable operation of power supply system and reduce the necessity of system overdimensioning. The following diagram presents the preliminary modelling results of DC based system operation with and without power smoothing.

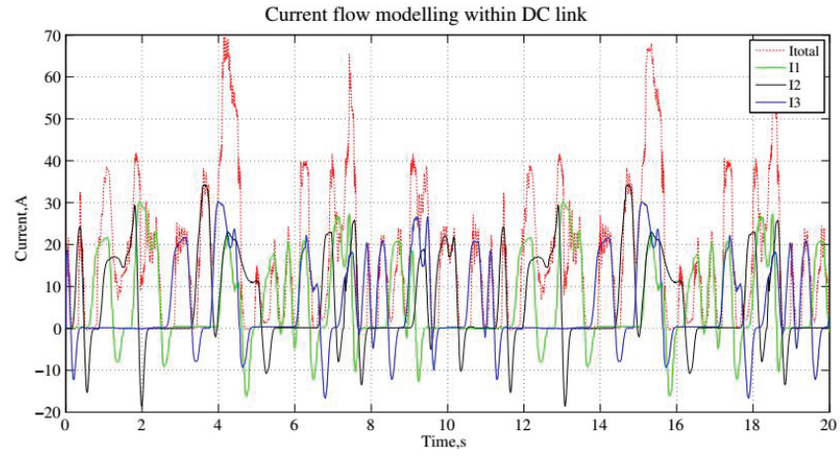

Fig. 4. *Current flow modelling within DC link*

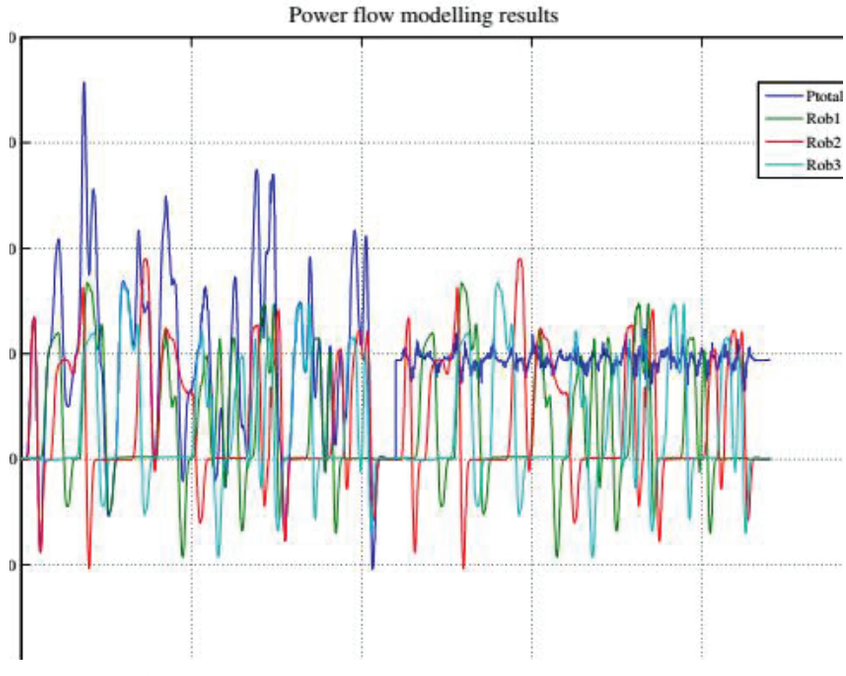

Fig. 5. *Power flow modelling results*

Fig. 5. represents two cycles of operation, each being 11 second long. Operation of 3 load elements representing the industrial robots has been modelled. Blue line represents the total power being taken off from AC grid and converted to DC for further distribution within DC link connection. First operation cycle does not incorporate any kind of energy storage utilisation and power taken from AC grid is a superposition of 3 load power variations. The other cycle starting after 11 seconds represents a prospective operation with supercapacitor unit as an energy storage element that is able to store or deliver power according to given reference value. Additionally, an inaccuracy has been introduced representing the communication time delays that typically lasts about 10 milliseconds in industrial *Profinet* protocol based network. The results show that stable enough power flow matching the sum of three robot consumed electrical power being 9 kW has been obtained by utilisation of energy storage.

Smoothing of total AC drawn power with respect to time has been observed, supporting the concept of power smoothing application by means of DC based microgrid. Such application would enable to consume the average power over a certain operation cycle and reduce short-term system overloads as well as enable lower margin for overdimensioning and respective investment costs

CONCLUSIONS

Within AREUS research project activities, new DC power supply concepts will be applied and demonstrated at Riga Technical University, Institute of Industrial Electronics and Electrical Engineering. Modelling with respect to anticipated electrical load power flows has been carried out for selection and design of DC system protection equipment, which is one of challenges due to lack of existing standards and market products for DC applications. Smart operation concepts in relation to smooth power flow control have been modelled, providing promising results. Further hardware implementation is planned as RTU demonstration facility will be equipped with experimental and measurement equipment.

ACKNOWLEDGMENT

The research leading to these results has received funding from the European Community's seventh framework programme under grant agreement no. 609391 (AREUS — Automation and Robotics for European Sustainable manufacturing).

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KOPSAVILKUMS

Rīgas Tehniskās universitātes Industriālās elektronikas un elektrotehnikas institūtā tiek realizēts ES FP7 Ietvarprogrammas projekts AREUS — Automatizācija un Robotika Ilgtspējīgai Eiropas ražošanai.

Projekta ietvaros laboratorijā tiek veidots jauns līdzstrāvas enerģijas sadales un apmaiņas infrastruktūras paraugs, ar kuru var pētīt dažādas automatizētu ražotņu enerģijas nodrošināšanas un vadības koncepcijas. Ņemot vērā tipiski industriālu robotu darbības režīmus, tiek modelēta jauna sistēma, kuras darbība tiks pārbaudīta, izmantojot elektriskās piedziņas stendus un industriālo robotu iekārtas, kas darbojas ar līdzstrāvu un apvienotas ar enerģijas uzkrāšanas iekārtām, augstākā līmeņa procesu vadības sistēmām un industrijā lietotām informācijas apmaiņas tehnoloģijām.

INSTITUTE OF MATERIALS AND STRUCTURES

Department of Composite Materials and Structures

Chair of Building Materials and Wares

OPTIMISATION OF THE CAR PART FROM GF/PP COMPOSITES

***Faculty** of Civil Engineering*

***Institute** of Materials and Structures*

►M. sc. ing., researcher
Edgars Labans

►Dr. sc. ing., leading researcher
Kaspars Kalnins

Volvo Group Trucks Technology, 405 08 Göteborg, Sweden

►***Philippe Lefort***

ABSTRACT

Design and optimisation of cargo truck cabin seat plate have been carried out in current research. In particular study, a traditional steel sheet material has been replaced by thermoplastic glass/polypropylene composite. Such design enables a possibility of quick one-shot manufacturing of composite structure and also provides a significant weight saving. The load case corresponding to the car crash seat pull test according to ECE-R14 standard has been applied for selection of material saving and for additional reinforcement. Topology optimisation results indicated areas where the volume of material should be increased or, conversely, decreased. In the following stage, parametrical optimisation of discrete number of reinforcement areas has been performed.

***Keywords**: thermoplastic composites, numerical modelling, optimisation.*

INTRODUCTION

Thermoplastic composites with woven glass/fibre (GF) and polypropylene (PP) fibres have demonstrated exploitable potential as valuable alternative to sheet metal providing a good strength/weight performance ratio (1). At the same time, mechanical properties of the thermoplastic composite are similar to those of traditional glass fabric laminates with epoxy resin matrix; however, manufacturing time advancing to extremely fast by hot mould pressing. Taking into account that the limit stress of thermoplastic composite (σ_x = ~350 MPa) (2) is close to the steel yield strength (for example, for S355 steel grade f_y = 355 MPa), such material could be successfully used for replacing metallic parts, for example, in truck cabin. Usually, sheet metal is applied for these needs due to convenient manufacturing process of cold stamping. However, taking steps towards introduction of composites requires an additional complicated manufacturing of hot moulds for detail forming and complex temperature control during processing. In addition, draping aspects should be considered to avoid wrinkles on component edges.

The present study is devoted to optimisation of material layout for the seat plate according to given loads and boundary conditions. It is especially important because fibre reinforced material could be tailored accordingly to the largest stress directions, strengthening the particular areas with additional fibres or locally adding 3D stiffeners for increasing the total height or thicknesses of the fabric, which could not be done with metallic parts in one-step manufacturing process.

Interpretation of obtained topology optimisation results usually brings about debates between scientists and engineers. Manufacturing constraints often limit the physical realisation of the optimal model and trade-off between optimality

and manufacturability should be found (3). *Currently a significant research attention is devoted to automatic converting of topology optimisation results into the CAD models. In semi-automatic approach to creation of parametrical models offered by* Larsen (4), the edges of eliminated volumes in optimised structure are replaced by predefined geometrical shapes with the small number of variable parameters. Earlier attempts were made in approximating the edges of topology plots with the spline curves (5) or modifying the cloud of points (6) in order to make the surface more uniform. However, these approaches have limitations on complexity of studied structure representation and require a human quality control to be implemented in design practice. Therefore, current industrial standard for processing topology optimisation plots is still a manual interaction by engineer.

OPTIMISATION USING TOPOLOGY PLOTS

Topological optimization is known as a shape optimization based on the principle of searching for the best material utilization to fulfil an objective criteria (in this case global stiffness) with respect to a given constraints (volume reduction). Topology plots allow to assess the approximate material distribution on the shell surface, which is useful to know in early stages of the product design. Although this may not be sufficient for entire development stage of a functional product, suitable for robust manufacturing. Reinforcement areas should be continuously discretized and at the same time made uniform with a minimal number of thickness variations, or the material trimming at all should be considered. Figure 1 shows the sequence for acquisition of the final design employing topology and parametric optimisation proposed in current paper.

Here the loading, geometry and boundary conditions are considered as input parameters for creating the topology plots on the top of initial geometry. Several cases of reinforcement patterns have been considered with slightly different distribution of reinforcement areas. In addition, the fields of load application were made of even thicker layer than the rest of the component. This allowed to save the material applying only required volumes of laminate at most stressed points and keeping the remaining area of the structure at relatively low thickness.

Convenient approach of determining the most effective thickness of reinforcement areas is to set these thickness values as parametrical variables and to optimize the structure in order to find the minimal thicknesses withstanding the stress and buckling restraints. Metamodelling technique could be successfully employed to solve this problem with minimal amount of trial runs. Even larger saving of the material volume could be reached introducing several sets of areas with variable thicknesses, although mathematical complexity will affect the manufacturability as well. If all conditions are satisfied, the component design could be considered as finalized from strength and stiffness point of view. Later modifications are only necessary if some manufacturing difficulties occur.

FINITE ELEMENT ANALYSIS

VISUAL CRASH-PAM (by ESI Group) finite element code has been employed to process the input files of the structure geometry and to formulate the loads and boundary conditions. CRASH-PAM is considered a convenient tool for solving static and dynamic tasks (7). The boundary conditions have been applied to perimeter nodes of the lower edge, restricting the translations in all three directions. The applied loads have been obtained from the automotive seat pull test according to ECE-R14 standard. According to this standard, the mass of the driver and the seat increases several times during extreme braking or crash.

Table 1. *ECE R14 standard load cases*

	$N_1(m < 3.5t)$	$N_2(3.5 < m < 12\ t)$	$N_3(m > 12\ t)$
Shoulder Block	13.5 kN	6.75 kN	4.5 kN
Lap Block	13.5 kN	6.75 kN	4.5 kN
Seat	20*x* seat weight	10*x* seat weight	6.6*x* seat weight

In such a way, the horizontal pull force (inclined 10 degrees upwards) is transformed into the vertical force while the horizontal components are acting on the seat connection points (Figure 2). To decrease the task complexity and avoid modelling, the whole seat structure forces acting on each support point have been derived from the full-scale truck model.

In front part of the structure the vertical load vectors are pointed downwards while the rear part`s loads are directed upwards (Figure 3). Depending on the vehicle class, two types of loads should be considered. In current study, a N2 class load scenario has been considered.

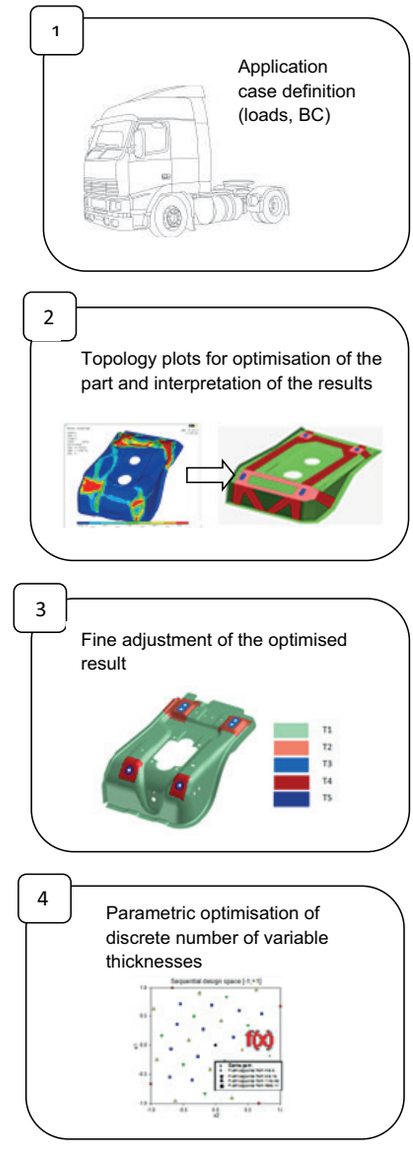

Fig. 1. *Workflow of the optimisation process*

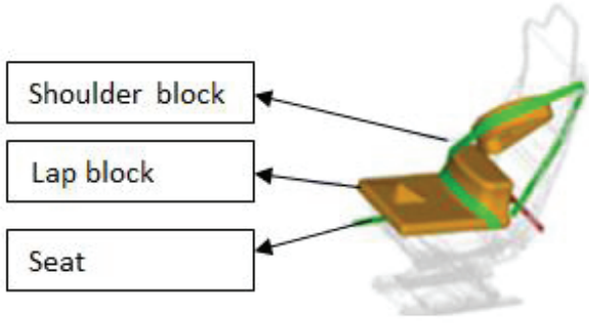

Fig. 2. *Load appliance scheme*

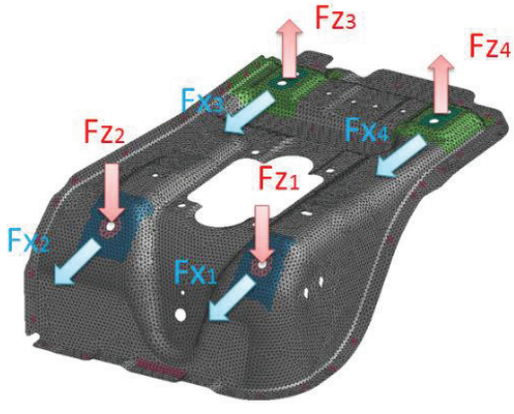

Fig. 3. *Structure mesh and load vectors acting on seat plate support points*

ANSYS (8) Shell93 type element with six degrees of freedom per node has been selected for the topology optimisation task. The employed element has an isotropic structure with material properties selected close to polypropylene/glass fibre laminate [1] of E_x = 20.7 GPa, E_y = 18.2 GPa, G_{xy} = 3.3 GPa and Poisson's ratio of 0.13.

TOPOLOGY OPTIMISATION PLOTS

Volume distributions at volume restraints have been analysed (Figure 4.). Blue colour shows areas where the material should be taken off, and red — where it should be left.

It may be clearly identified in all plots that the least stressed part of the structure is the centre where the material should only be left for non-structural purposes. The largest material volume — thickness — should be left under the loading points. These critical areas are recognizable in both initial and simplified geometry plots. Several strategies could be adopted to reinforce the most stressed areas.

One of the strategies was the embedding of additional yarns or fabric layers locally, while taking into consideration that the composite materials are more effective in topology optimization tasks than the isotropic materials (9) it could be the least sophisticated way of local part reinforcement. Other option is implementing the stiffness ribs according to the stiffener pattern that could be identified in the volume distribution plots with 50 % and 70 % volume restraints. In this case, the horizontal stiffeners will link all loading spots and the vertical ribs will reinforce the front edges.

The acquired knowledge about the material distribution will further serve as the starting stage for further development of functional product, involving feasibility studies of introducing the rib stiffeners or other three-dimensional reinforcing elements made of thermoplastic textile composites.

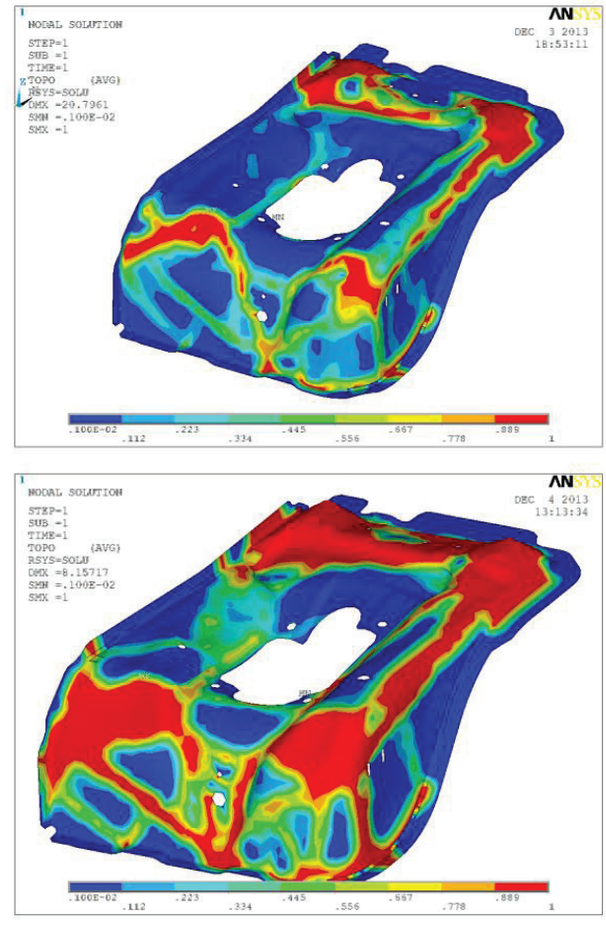

Fig. 4. *Volume distribution in structure at various volume restraints*

PARAMETRICAL OPTIMISATION OF REINFORCEMENT AREAS

In order to demonstrate the possibility to strengthen the composite seat plate locally, shell areas with thicker zones have been introduced. Locations of thicker reinforcement areas have been identified following the main stress directions and information obtained from the topology plots. Primary load bearing areas have been placed in the vertical zone, starting from the skew plane load appliance points down to the structure baseline. Rear areas of the part have been reinforced in the same way. Moreover, the additional thickness property has been assigned to the load appliance points to avoid the local stress concentration.

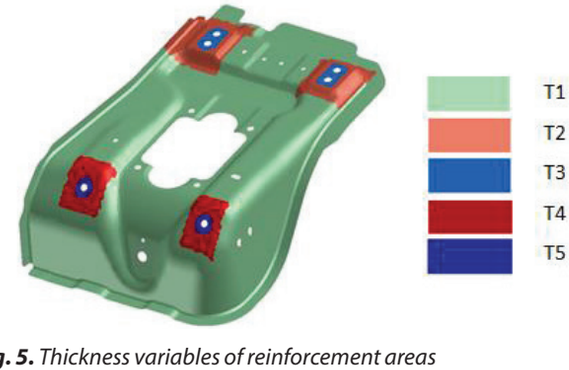

Fig. 5. *Thickness variables of reinforcement areas*

In present research, a sequential space filling design based on Latin Hypercube with the mean-square error criterion has been employed. Design of the experiments has been created in EdaOpt in-house software (10). Lower boundary for thickness variable has been assumed 3 mm and upper — 7 mm. The acquired responses have been approximated by ABFC method in VariReg software. Volume approximation function has been minimized to found the least value in relation to maximal stresses in GF/PP composite (11). The results of parametric optimisation are shown in Table 2. Although the composite part has larger thicknesses, it still maintains less than a half of weight of initial steel structure.

Table 2. *Optimal thicknesses distribution of the seat plate*

Design case	Material	Number of variable thicknesses	Relative volume of the structure (N2 load case)	Relative mass of the structure
Initial 	Steel	1	100 %	100 %
Optimised structure 	GF/PP	5	189 %	35 %

CONCLUSIONS

During the present research, the advantages of employing the topology optimisation in design of truck cabin seat plate made of thermoplastic GFRP composite have been investigated. The results of topology optimisation demonstrated that at early stage of the part design a special treatment should be made in relation to the load appliance points where significant local stresses occurs. The most perspective solution of this issue is the creating of 3D woven or knitted fabrics with initially added thicknesses at the most stressed areas. To elaborate the required shell thicknesses, a parametrical model was created based on the topology optimisation results.

Employing the parametrical FEM model, it was found that the thermoplastic laminate material had a potential of ensuring the required strength properties at the same time keeping the thickness at reasonably low level. Although thicknesses of the fibre composite shell exceeds that of the initial steel part, low density of GF/PP material allows reducing the weight of the reference steel part by 75 %.

Further work will be done to improve the reinforcement pattern at seat connection, thus reaching even more weight saving.

ACKNOWLEDGEMENTS

This study has received a support from the European Commission through the large-scale integrating collaborative project MAPPIC 3D — number 263159-1 — and entitled: One-shot Manufacturing on large scale of 3D up graded panels and stiffeners for lightweight thermoplastic textile composite structures.

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KOPSAVILKUMS

Tradicionāli auto ražošanā kabīnes izgatavo no metāla. Lai šo procesu varētu optimizēt, tiek pētīta auto kabīnes detaļas izgatavošana vienā paņēmienā no stiklašķiedras un polipropilēna termoplastiskā kompozīta. Šī materiāla izmantošana ļauj samazināt konstrukcijas masu, salīdzinot ar tradicionālo metāla izstrādājumu. Detaļa tika pārbaudīta, pieliekot slodzi, kas noteikta sēdekļa izraušanas testa ECE-R14 standarta prasībās. Lai noteiktu apgabalus, kuros jākoncentrē lielākais materiāla daudzums, tika izmantoti topoloģiskās optimizācijas paņēmieni. Galīgais pastiprinājuma laukumu biezums tika iegūts, izmantojot parametrisko optimizāciju.

INNOVATIVE MATERIALS FOR THE EFFICIENT BIOGAS PRODUCTION

***Faculty** of Civil Engineering*

***Institute** of Materials and Structures*

***Department** of Water Engineering and Technology*

►Dr. sc. ing., Prof.
Diana Bajare

►Dr. sc. ing.
Kristine Rugele

►Mg. sc. ing.
Ģirts Būmanis

ABSTRACT

The use of secondary raw materials (waste) for production of innovative products for renewable energy systems is a very attractive topic in the terms of sustainable development. The successful research and development of a new material for sustainable and affordable low carbon energy technologies, particularly for advanced biogas production technology, is a very complex and multidisciplinary challenge having technical, ambient, financial, marketing, legal and social aspects.

In this research alkali activation of industrial waste was performed. The novel material contains up to 50 % of secondary raw materials (industrial waste from aluminium scrap recycling and waste glass) and local raw materials. Materials with high porosity and buffering capacity, and long term alkali diffusion, are integrated into biogas reactor system for simplified process operation and control.

***Keywords**: alkali activated materials, industrial waste, buffer capacity, biogas production.*

INTRODUCTION

During the last few decades, there has been a growing interest in alternative forms of energy One of the most promising alternative energy types is biogas. Whey, which is the main pollutant in dairy industry, represents a potential energy source and anaerobic digestion offers an excellent approach in terms of both energy conservation and pollution control. However, whey anaerobic treatment is usually unprofitable due to the high energy cost and the complexity of the process. Whey is characterized by a very high organic load and low buffer capacity; consequently, the direct anaerobic treatment of the raw whey can lead to rapid acidification which results in low biogas productivity, therefore supplemental alkalinity is required to avoid anaerobic process failure [1]. Apart from automated online pH control, the pH instability in the anaerobic digestion systems can be controlled via addition of alkaline materials. The addition of alkaline materials (AAM) to anaerobic digestion process makes it more stable and faster, so it is possible to operate batch type and continuous reactor system at higher whey loading rate [2, 3]. During the material formation process, in its structure is incorporated a certain amount of alkalis, which is not used during the synthesis (polymerization) process of the material. After solidification of the material, the alkaline compounds are crystallizing on the walls of pores in the form of crystalline formations (Figure 1).Material dissolves base in aqueous solutions thus providing the increase of pH. Due to partly closed pore structure, base is

emitted gradually thus ensuring the long — term process, which is associated with alkali diffusion from deepest layers of the material.

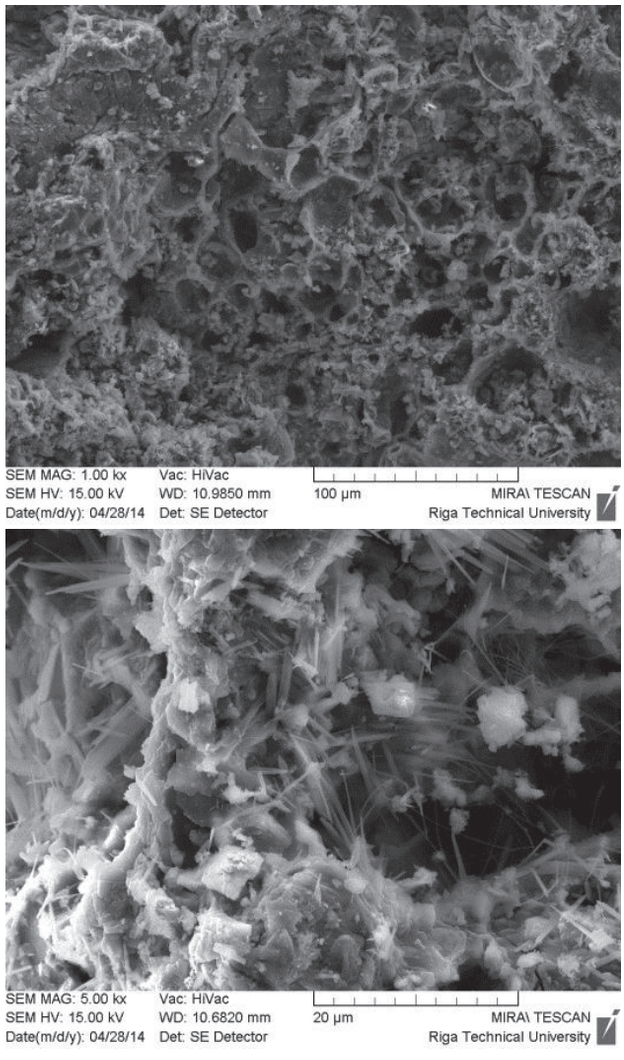

Fig. 1. *AAM SEM micrographs: a) 100x magnification, b) 5000x magnification*

RESULTS

Different types and proportions of raw materials are used therefore ratios of oxides SiO_2/Na_2O, SiO_2/Al_2O_3 in the composition also change, which, in turn, determines the alkali diffusion intensity and ambient pH regulation capability (Figure 2). The thermal tratment of samples within temperature range 200–400 °C allowed to reach an effect when the alkali diffusion from the material structure is highly gradual even within up to 70-day long period (Figure 3), thus ensuring a sustainable ambient pH level within the interval 8.5 and 10.5 (Figure 4).

After 70-day long pH test, the alkali diffusion from AAM structure is still possible, which is proved by SEM micrographs (scanning electronic microscope, Figure 5).

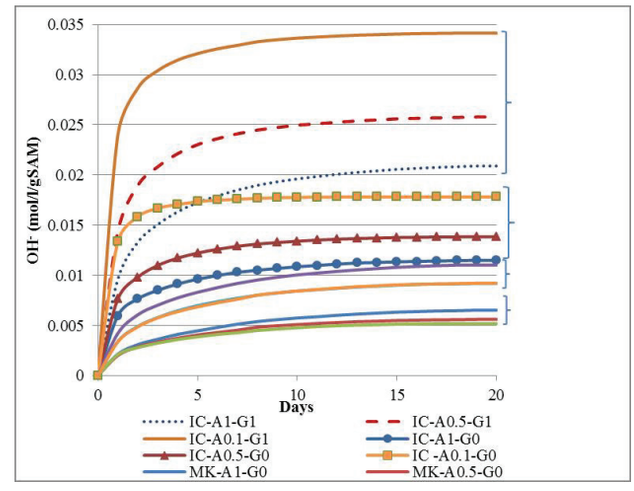

Fig. 2. *OH- ions leaching from AAM produced on the base of calcinated illite (IC) or metakaolin (MK) with or without glass additive (G) in compound and with different quantity of pore-forming additives (A)*

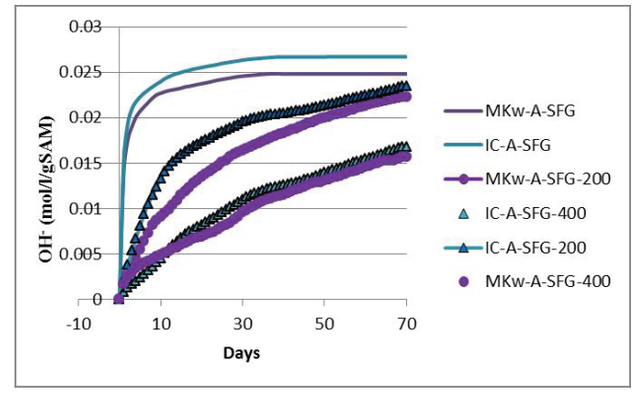

Fig. 3. *OH- ions leaching from AAM structure produced on the base of calcinated illite (IC) or metakaolin (MKw) with or without glass additive (SFG) in compound and thermally treated at temperature 200 °C or 400 °C*

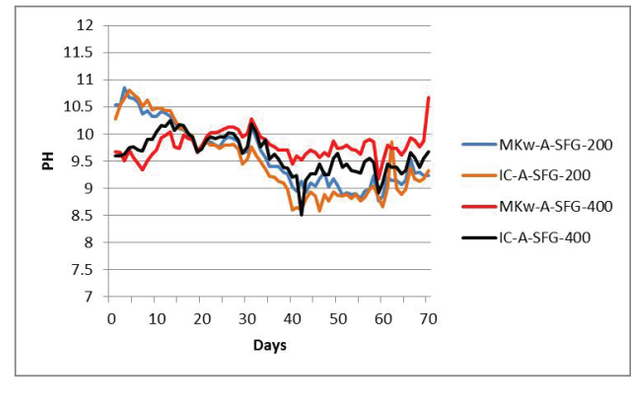

Fig. 4. *pH level for water solution after AAM immersion. AAM based on calcinated illite (IC) or metakaolin (MKw) with or without glass additive (SFG) in compound and thermally treated at temperature 200 °C or 400 °C.*

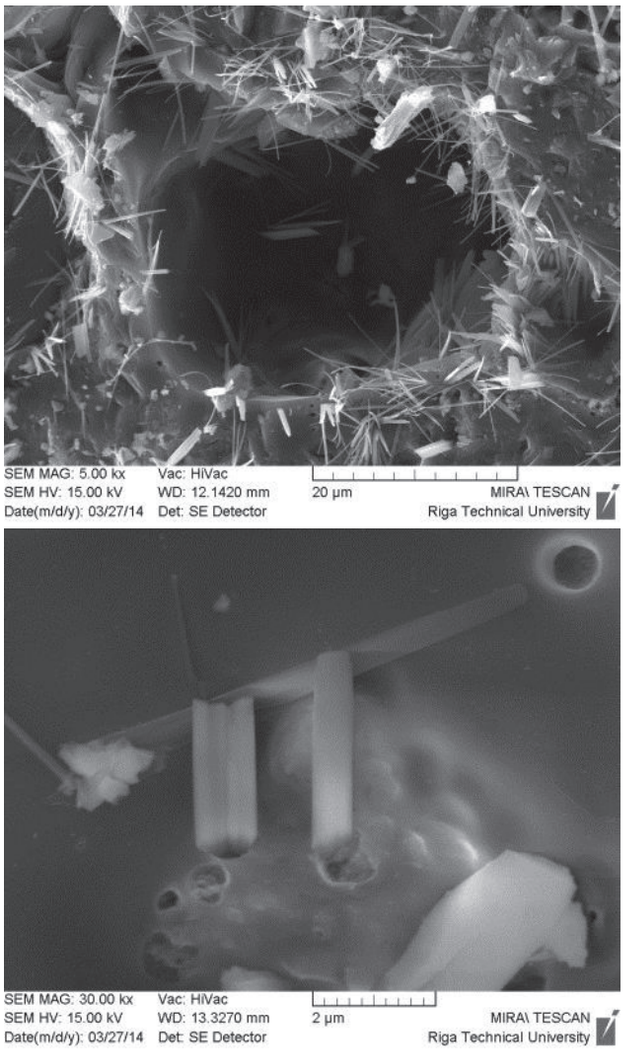

Fig. 5. *SEM micrographs of AAM after 70-day long pH test; crystalline forms are still visible on AAM pore surface (5,000x and 30,000x magnifications)*

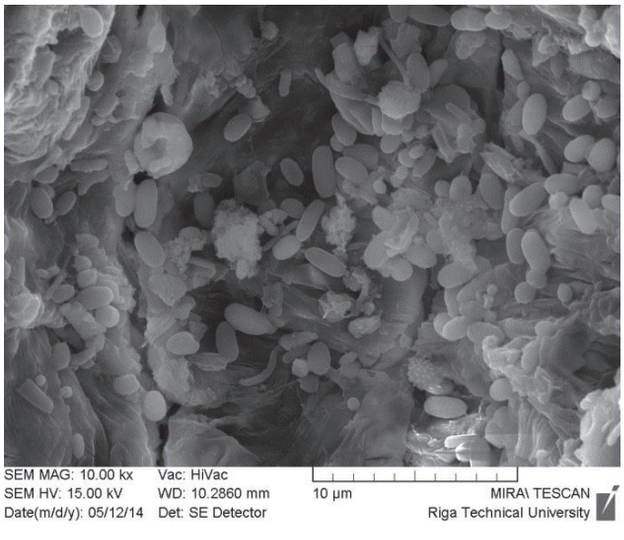

Fig. 6. *Immobilization of microorganisms on AAM surface (SEM micrographs, 10,000x magnification)*

AAM can be efficiently used for regulation of pH level. Buffer capacity may be influenced by the size of AAM granules, what is the one of the most important factors to control OH^- ions diffusion kinetics and intensity.

It was also demonstrated that biofilm was present on the granules at the end of the experiments. In present study during cultivation over 30 days, two dominant cell morphologies were observed — coccoid form with dimensions of approximately 0.6 µm in diameter and rod-shaped forms in length of approximately 2 µm similar to those observed in the initial inoculum (Figure 6).

CONCLUSIONS

Alkali-discharging materials from aluminium and glass recycling waste can be used as new progressive materials both for pH control and also as substrates for immobilization of microorganisms in anaerobic digestion processes.

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KOPSAVILKUMS

Pieaugot primāro energoresursu pieprasījumam, aizvien izplatītāki kļūst jaunu alternatīvu enerģijas resursu meklējumi. Viens no perspektīvākajiem alternatīvajiem enerģijas avotiem ir biogāze. Piena pārstrādes industrijas blakusprodukti, piemēram, piena sūkalas, ir potenciāls atkritumprodukts, kuru varētu efektīvi pārstrādāt biogāzē, tomēr ieguves zemā efektivitāte un augstās izmaksas bremzē plašu tehnoloģijas izmantošanu. Viena no galvenajām problēmām sūkalu pārstrādē ar anaerobo baktēriju palīdzību ir vides paskābināšanās ražošanas procesā, jo sūkalām ir zems pH līmenis (<6). Šī problēma ir īpaši aktuāla vienpakāpes nepārtrauktas darbības reaktoros ar augstu organisko daļiņu saturu un tvertnes tipa reaktoros, tādējādi šādās sistēmās nepieciešams veikt pH regulāciju. Sārmu aktivizēto materiālu struktūrā jau materiāla veidošanās procesā tiek ieslēgts noteikts daudzums sārma, kas netiek patērēts materiāla sintēzes (polimerizācijas) procesa laikā. Pateicoties materiāla daļēji slēgtajai poru struktūrai, sārmu izdalīšanās šķīdumā notiek pakāpeniski. Tā rezultātā tiek nodrošināta ilglaicīga vides pH paaugstināšana/stabilizēšana, kas saistīta ar koncentrācijas gradienta izraisīto sārma difundēšanu no materiāla dziļākajiem slāņiem.


INSTITUTE OF BUILDING ENTREPRENEURSHIP AND REAL ESTATE ECONOMICS
Department of Civil Construction and Real Estate Management
RTU Scientific Research Laboratory of Building Entrepreneurship and Real Estate
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SPECIFICATION OF THE DEVELOPMENT PATTERN FOR NANOTECHNOLOGY IN LATVIA

***Faculty** of Engineering Economics and Management*

***Institute** of the Civil Engineering and Real Estate Economics*

►Dr. oec., Prof.
Ineta Geipele

►Dr. oec., Prof. asist.
Tatjana Staube

►Dr. oec., Prof. asist.
Guna Ciemleja

ABSTRACT

The authors prepared this paper on the basis of the Staube et al., 2014 [1] publication accepted for the 1st international scientific conference on advanced materials, structures and mechanical engineering ICAMSME 2014, which took place in Incheon, South-Korea on May 3–4, 2014 and included into the international scientific journal "Advanced Materials Research". Among the main findings, the authors created a diagram of the development of legal environment for the advanced technologies according to a time scale. From official documentation the authors concluded that despite the nanotechnologies were announced in the second priority for development of the Latvian science, and Latvia had a very high rates of an international collaboration (70 %) and EU support to the scientific projects (about 77 % from total investments): 1) our state was not named among the priority regions in the newest EU's smart specialisation platform; 2) obvious limitations in local tooling and professionalism caused our country to still stay at the foundation stage.

***Keywords**: advanced technologies, emerging technologies, innovation, legal environment for the advanced technologies in Latvia, nanotechnology in Latvia, smart specialisation.*

INTRODUCTION

The authors proposed an unbiased approach to get a review of the nanotechnologies evidence issue in the Republic of Latvia from the scientific literature (including ISI Web of Science, SCOPUS scientific databases), official statistics and professional analytical reports (including local and European statistics, professional databases) and official documentation in Latvia and European Union relying on the existing terms and definitions [1]. A focus on the local documentation through integration into the European Union is accepted limitation of the Paper.

In the scientific and professional literature, a great attention is paid to the "analysis of emerging technologies" [2] or "advanced technologies". According to the official analytical information, global demand for nano-materials is expected to grow up reaching almost 6 billion US dollars by 2016 that makes a wide margin since 2001 [3]. The global nanotechnology market is anticipated to expand at a compound annual growth rate of around 19 % during 2013–2017 [4]. The Americas, Asia and Pacific regions are reported to keep the leading regional position in dominating a demand, and the fastest growth is expected in Eastern Europe, Africa and Middle East [3]. The authors have made investigation on the Republic of Latvia as a part of the Eastern European contribution. According to

the official documentation, the main tasks set for science in Latvia include the establishing ground for the development of new technologies and their implementation mechanisms. Basing on these data and from the analytical results presented below, the authors found that within the last decade Latvia is still at the foundation stage.

RESULTS AND CONCLUSIONS

The authors found certain correlation in the development of the political platform, scientific activity, increase of international funding, and dynamics of the expenditure on Research and Development (hereafter R&D) in the Gross domestic product and, as a result, a share of local scientific papers devoted to the advanced technologies in a total number of scientific articles. As shown on the graph below (Fig. 1), the actual activity of the scientists is sequential with financial granting.

To achieve a better coordination of Latvian economic policy, the Entrepreneurship competitiveness and innovation programme for the period 2007 to 2013 was approved by the Cabinet of Ministers of Latvia in the middle of 2007 (Fig. 1). It became an umbrella document uniting the former government policies and the planning papers. The priorities are revised once every *four years*. In 2013, the Ministry of Education and Science has approved six priority branches of science for the period 2014–2017. Innovative and advanced materials, smart technologies connected with nanotechnologies, informatics, information and signal-processing technologies have been moved to the second priority [5].

Within the period 2002 to 2005, the accumulated amount of investment in support of the nano-related projects counted 5.5 million euros. Since 2005, a significant increase has been marked in further investments into scientific projects with participation of local scientists. A total projects financing from 2002 to 2017 where the leading Latvian scientific institutions participate is over 31 million euros [6]. It might be even higher, but the authors have not yet included the newest project proposals of the New Horizon 2020. Here, the average share of the European Union's financial support of Latvia amounts to 77 % from the mentioned sum, which evidences a high rate of international collaboration in nano-science generation of Latvia. This figure was about 70 % on average within the last eight years [7].

A share of the indexed nano-articles in total scientific articles of a country in ISI Web of Science scientific database marked in the above diagram as a local share in nano-science generation, is ranking Latvia with a positive dynamics from 4.46 in 2000 to 10.68 in 2013. Our country holds comparatively high position in this category. For instance, South Korea — 15.61, Lithuania — 7.51, USA — 6.36, Estonia — 6.28 (2013 rankings).

Since 2013, Latvia is a participant of the Research and innovation strategies for smart specialization or RIS3 within the Smart Specialization Platform for the Baltic Sea region in the EU. However, Latvia was not included in the list of the declared priorities' regions for KETs within RIS3 platform [9]. According to the RIS3, the knowledge-based development has to be maximally combined with qualified human capital within the fields where Latvia has advantages and which are important during the process of transformation of National Industry.

Latvia occupies low 68th place in the Global Competitiveness Index 2012–2013 by World Economic Forum after evaluation of innovations level in 144 states. Inadequate situation in the field of Intellectual Property Protection

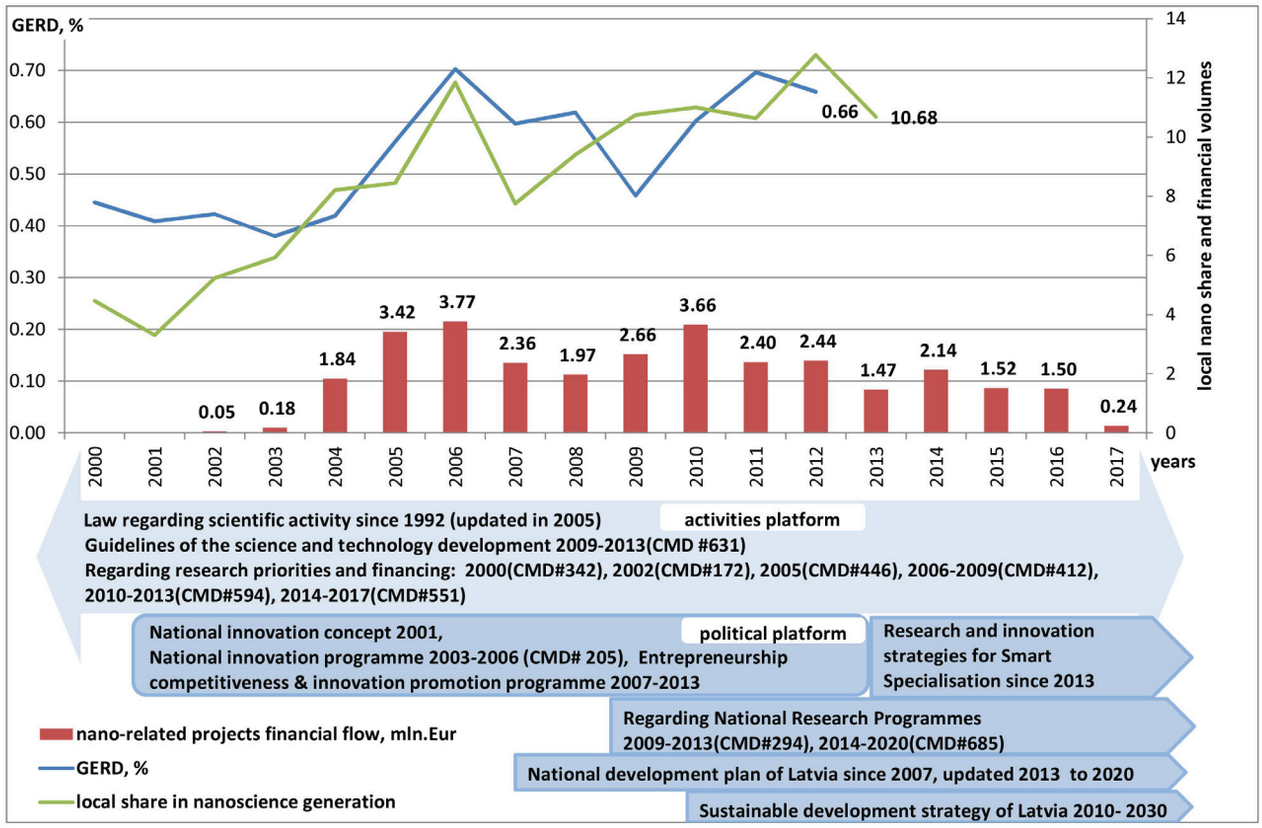

Fig. 1. *Development of legal environment for the advanced technologies in Latvia [1, 5–8].*

placed Latvia the 60th [10]. In 2012 Latvia has improved its position in the International Property Rights Index. Deficiencies of the system are creating the lack of originating of inventions, because the patent system is not friendly for inventors and economically unjustifiable, and case law is unpredictable and jurisprudence not consistent [11]. Furthermore, the authors marked the incompatibility in official statistics on the nanotechnology patents registered in Latvia. According to the industry analytical Scoreboard's information, since 2000 Latvia was granted three nanotechnology patents in the European Patent Office: in 2010, 2011 and 2013 (for comparison, Lithuania has three, and Estonia — four granted patents in EPO) [7, 12]; since 2009 there is one registered patent in the World Intellectual Property Organization database [13], and eight granted patents in the database of the European Patent Office [14]. Low innovation level in Latvia proves that the existing innovation system has shortcomings. Nationally identified drawbacks are associated both with every individual element of the innovation system and with their interaction [15]. The Cabinet of Ministers approved the objectives until 2020, namely, modernisation and integration of the science, creation of a demand for innovations, increase in compatibility of local science and development of human capital in innovations and technology [5].

ACKNOWLEDGEMENTS

ESF EIROPAS SOCIĀLAIS FONDS
IEGULDĪJUMS TAVĀ NĀKOTNĒ

This work has been supported by the European Social Fund within the project "Development of multifunctional nanocoatings for aviation and space techniques constructive parts protection" No. 2013/0013/1DP/1.1.1.2.0/13/APIA/VIAA/027

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Doto rakstu autores ir sagatavojušas, par pamatu ņemot Staube *et al.*, 2014 [1] publikāciju, kas pieņemta ICAMSME2014 ietvaros (pirmā starptautiskā zinātniskā konference par inovatīviem materiāliem un struktūrām mašīnbūves jomā, kas notika Inčhonā, Dienvidkorejā 2014. gada 3. un 4. maijā), kā arī minētā publikācija ir iekļauta starptautiskajā zinātniskajā žurnālā "Advanced Materials Research". Viens no jaunākajiem pētījuma rezultātiem ir autoru izstrādātā tiesiskās vides attīstības diagramma, kas attēlo nanotehnoloģiju jomas atbalstu Latvijā, pielietojot laika skalu. Zināms, ka nanotehnoloģijām Latvijas zinātnes attīstībā ir piešķirta otrā prioritāte un mūsu valsti raksturo augstas starptautiskās sadarbības likmes (70 % apmērā), kā arī ES atbalstītā zinātnisko projektu realizācija ir ap 77 % no investīciju kopapjoma. Tomēr, neskatoties uz iepriekšminēto un analizējot oficiālo dokumentāciju, autores secināja, ka 1) ES viedās specializācijas platformas jaunākajā redakcijā Latvija netiek minēta starp prioritārajiem reģioniem; 2) pastāv acīmredzami vietējo iekārtu un profesionālās kapacitātes ierobežojumi, kuru dēļ mūsu valsts nanotehnoloģiju joma tiek novērtēta kā esoša attīstības sākuma posmā.

Information provided by Faculties and Institutes of RTU and compiled by
Department for Research Coordination and Information

English proofreading Genadijs Bukatovs
Publishing project Manager Natālija Čina
Computing Designer Jekaterina Ribajeva
Cover Designer Jekaterina Stakle, jekaterina.stakle@gmail.com

Published by RTU Press, Riga Technical University
1 Kalku Street, Riga, LV-1658
E-mail: izdevniecība@rtu.lv

Printed by RTU Printing House