Bilateral Cooperation Program between Romania and Korea

FINAL RESEARCH REPORT

Project „THIN FILM OF NANOPOROUS SILICA ZEOLITE CRYSTALS ON CERAMICS FOR LOW-DIELECTRIC CONSTANT MATERIALS" -FILOWEPS-

- Contract no: **64CB/04.07.2008**
- Web page: **www.loweps.ee.tuiasi.ro**
- End year: **2009**
- Duration of the Bilateral Project**: 17 months**

- Romanian Partner: **The "GHEORGHE ASACHI" TECHNICAL UNIVERSITY of IASI**
- Head of Institution: **Rector Prof. Ion GIURMA, Ph.D Eng.**

- Project manager: **Prof. Romeo Cristian CIOBANU, Ph.D Eng.**

- Foreign Partner : **HANSEO UNIVERSITY, Korea**
- Head of Institution: **President Kee Sun HAM**, **Prof. Ph.D**

- Project manager**: Prof. Ik Jin KIM, Ph.D Eng.**

November 2009

DESCRIPTION OF THE PROJECT

The **„Thin Film of Nanoporous Silica Zeolite Crystals on Ceramics for Low-Dielectric Constant Materials”** Bilateral Project, financed through CAPACITIES Programs, Module III, bilateral cooperation carried out in collaboration with the University of HANSEO, South Korea proposes the development and manufacture of ceramic thin films of nanoporoase zeolites crystal silicon on glass and ceramic substrate materials with low dielectric constant. A nonoporous silica zeolite thin film which is one of the decisive candidate materials for future generation low-dielectric constant materials. A lower dielectric constant materials can reduce resistance capacitance (RC) delay, power dissipation, and interline crosslink. Organization of nanometer-sized zeolite crystals into uniformly oriented monolayers on various supports by hydrothermal method is of great interest for various reasons. For instance, it is an effective way to produce zeolite thin film that can be widely applied in industry as thin-film catalysts, nano-porous sieves for molecular separation, size-selective sensing devices. The oriented monolayers thin film of zeolite crystals have also great potential as ideal media for organization of semi-conductor quantum dots and nonlinear optical molecules, and as well-defined nanoreactors for exploration of novel chemistries in highly confined and organized environments.

The project becomes essential for literacy development in the field, and is in line with new guidelines for broadband dielectric spectroscopy applications worldwide.

The level of dissemination of the project is extended, including the website (www.loweps.ee.tuiasi.ro), publications, organization of round tables and workshops, promoting results within international networks to which team members are partners.

PARTENERS

Korean partner – **Hanseo University**, one of the most experienced institute in the field - contributed with basically and technical characteristic analysis by using Environmental Scanning Electron Microscopy (ESEM), High Resolution Transmission Electron Microscopy (HRTEM), X-ray powder diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, DTA/TGA and BET analysis, not fully available in Romania.

Romanian partner **– The "Gheorghe Asachi" Technical University of Iasi,** the most important department of advanced dielectric analysis in Romania - investigated the dielectric constant of the orientation-controlled monolayer assembly of zeolite nanocrystals on glass and ceramic substrates by covalent linkages. The used dielectric methods were: broadband dielectric spectroscopy up to 10 GHz and up to 450 C, pulse electroacoustic analysis, broadband partial discharges analysis and thermally simulated currents method, methods not fully available in Korea.

NECESSITY OF THE PROJECT

Nearly perfect crystalline zeolite structures are very important for a variety of studies. They aid in the fundamental understanding for the crystal structure, for use as such a micro reactor for model reaction, chemical sensor and host materials for semiconductor clusters. At sizes from 1 to 20 nm in diameter, they can create electronic and optical properties specific to the form of nanocrystals. Therefore, the synthesis of zeolite nanocrystals and the organization of these crystals into uniformly oriented monolayers on ceramic substrate by covalent linkage are of great interest for various reasons.

To allow research project to realize the organization of nanometer-sized zeolite crystals into uniformly oriented monolayers on various supports by covalent linkages, there were a need for broadly based, powerful action alliances to bring nano-porous sieves for molecular separation and size-selective sensing devices. In the proposed research initiated by Hanseo University and Technical University of IASI, were be together prepared uniformly oriented monolayers on glass or ceramic substrates by covalent linkages, also functional nanostructured molecular materials and these molecular graded materials were performance tested for many important applications for low-dielectric constant materials. It was also expected that this study will be help to determine the role of covalent linkages in self-assembly monolayer and also multilayers coating for better understanding of the coating mechanism. Our aim in side of Korea was to contribute to advance monolayer and multilayer assembly of nanometer-sized zeolite crystals on glass and ceramic substrates by covalent linkages to apply innovative nanodevices for next generation through an international cooperation.

GENERAL AIM

Organization of nanometer-sized zeolite crystals into uniformly oriented monolayers on various supports by hydrothermal method is of great interest for various reasons. For instance, it is an effective way to produce zeolite thin film that can be widely applied in industry as thin-film catalysts, nano-porous sieves for molecular separation, size-selective sensing devices.

A nonoporous silica zeolite thin film which is one of the intersecting candidate materials for future generation low-dielectric constant materials for semiconductor industry, the most commonly used dielectroic insulator in microprocessors is dense non-porous silica, which has a k value of about 4.0 A lower dielectric constant materials can reduce resistance capacitance (RC) delay, power dissipation, and interline crosslink. A viable low-k material must be compatible with multistep semiconductor integration processes such etching, stripping, cleaning, damascene lithography, and chemical mechanical polishing etc

The oriented monolayers thin film of zeolite crystals have also great potential as ideal media for organization of semi-conductor quantum dots and nonlinear optical molecules, and as well-defined nanoreactors for exploration fo novel chemistries in highly confined and organized environments.

In the frameworks of the project it was proposed to develop and fabricate the self-assembly of building blocks in the form of highly ordered arrays or thin films on glass and ceramic substrates. Zeolite nanocrystals of a uniform particle size between 60-130nm were synthesized by a hydrothermal method. The reactant materials used were aluminum isopropoxide $Al(i\text{-}pro)_3$ (Aldrich, 98wt%), tetraethylorthosilicate (TEOS, Aldrich, 98wt%), tetramethylammonium hydroxide (TMAOH, Aldrich, 25wt% in water), and sodium hydroxide (NaOH, Aldrich, 99.99wt%). The autoclave was removed at predetermined times from the oven to arrest the reactions. The crystallized samples were collected and separated by centrifugation. The products were repeatedly dispersed in distilled water using ultra sonication and centrifugation as above to remove the remaining mother solution until the pH of the dispersion was close to 7-8. (3-aminopropyl)triethoxysilane(APS, 99%), 1,4-diisocyanatobutane(DIC-4, 97%), (3-

choropropy)triethoxysilane(CPS, 97%), and Fullence(95%) from Aldrich were used as covalent linkages for self assembly monolayer between zeolite and ceramic substrates.
The study assumed a joint effort of students and scientists from ***Korea and Romania*** to investigate dielectric constant the orientation-controlled monolayer assembly of zeolite nanocrystals on glass and ceramic substrates by covalent linkages. The used dielectric methods are: Broadband dielectric spectroscopy up to 10 GHz and up to 450 C, Pulse electroacoustic analysis, Broadband partial discharges analysis and thermally simulated currents method.

PROJECT DISSEMINATION ACTIONS

TRAVEL ABROAD AT THE KOREAN PARTNER UNIVERSITY

During 25.10.2008-14.11.2008 a researchers team from Romania went to the **Hanseo University, South Korea** for a documentation and research visit to successful performance goals under the implementation plan. During the visit, the four researchers Marius Olariu, Cristina Bratescu, Ramona Burlacu and Alexandru Trandabat with the group of researchers from the host university have achieved the synthesis of silica and zeolite nanoporous nanocrystals and contributed to making nano-assemblies with predefined architectures, one of main objectives stipulated in the project implementation plan.

In October 2009 a team of Prof. Romeo Ciobanu, PhD Eng, Dean Prof. Alexandru Salceanu, PhD Eng, Prof.. Cristina Schreiner PhD Eng and Lecturer Alexandru Trandabăţ PhD Eng visited **Korea University**, where they held discussions on the obtained results in the project, promotion of new project proposals under the FP7 and signed a cooperation agreement between the two universities The"Gheorghe Asachi" Technical University of Iasi and the University of Hanseo, South Korea

PERFORMANCE OF VISITS TO ROMANIA BY KOREAN PARTNER:

During the visit to the first stage, Professor Ik Jin Kim from Hanseo University, South Korea participated along with others invited to the Workshop "Advanced Materials and Technologies from FP7 Bilateral Cooperation to Partnership" organized in collaboration

with our faculty, where he introduced new methods to synthesize the zeolite nanocrystals and discussed about the importance of obtaining thin films nanoporous of silica and zeolites. During his visit Professor Ik Jin KIM together with our team investigated the dielectric constant of nanocrystal assemblies of zeolite monolayer with controlled orientation on glass and ceramic substrate by covalent linkage using broadband dielectric spectroscopy up to 10 GHz and 450 C.

ORGANIZATION OF SCIENTIFIC EVENTS WITH INTERNATIONAL LEVEL IMPACT

With the last year registred success of the **Workshop "Advanced Materials and Technologies from FP7 Bilateral Cooperation to Partnership"** organized in Iasi, and because the scientifc event brought together experts who can apply the ideas directly from the currency of experiences, two research teams in Romania and Korea have decided to continue discussions and presentation of results obtained in a new workshops.
In this case **Professor Ik Jin Kim** attended along with other researchers from Romania and abroad to the **Workshop "From bilateral towards international cooperation-Advanced Ceramic Nanostructures"** held during 8-9.10.2009 in Iasi, dedicated to the dissemination of scientific results obtained in project. Scientific event was aimed at discussion of the main objectives of the project and present results, realizing it in a high professional framework in which specialists can invited to express views and opinions about the theme of the project.
Besides the above mentioned topics in the workshop, discussions have allowed the crystallization of issues of common interest, the directions of future cooperation, both between Romanian researchers and between researchers and the Romanians abroad, were discussed with support the participation of Romanian researchers in international research projects, expansion of international cooperation programs and projects, increasing access to research infrastructure performance and boost collaboration and participation in national and international networks.

PUBLICATIONS

The research results have been recovered by the publication of the two joint scientific articles in specialized journals

♦ **Self-Assembly Monolayer Coating of TMA-A Zeolite Nanocrystal on Glass by Covalent Linkages,** Young Mi Kim, and Ik Jin Kim , Marius Olariu, Alexandru F. Trandabat, and Romeo-Cristian Ciobanu, The Journal of Ceramic Processing Research indexed in SCI

♦ **Effect of interconnected molecular types on the packing rate of self-assembled monolayers of TMA-A zeolite nanocrystals on glass,** Ik Jin Kim, Wei Zhao, and Jeong Ho Chung, Marius Olariu, Alexandru F. Trandabat, and Romeo-Cristian Ciobanu

SUBMISSION OF JOINT PROJECTS

♦ FP7-PEOPLE-IRSES-2008 - "Nano-structured low dielectric materials based on zeolites by self-Assembly monolayer" with support from Korea Institute for the Advanced of Technology (KIAT)

♦ Teaching and research bilateral joint project in the field of: "Nano-structured ceramic low dielectric materials", in the agreement between universities 2009

TRAINING OF YOUNG RESEARCHERS AT DOCTORAL LEVEL

Amplification of the educational dimension of the project was achieved by integrating and support of young researchers and doctoral students, **the project having a major role in the doctoral thesis „Contributions to the quality analysis of electrical insulating materials by the dielectric spectroscopy method" by Mr. Aradoaei Sebastian, PhD Eng who was sustained in April 2009** and also representing **the starting point of the doctoral thesis** entitled **"Research on the use of ceramic thin films on substrates nanoporoase of zeolites crystals with low dielectric constant" prepared by Eng. Cristina Bratescu, PhD student, that will be underlie in September 2010**. The project aims rejuvenation of human resources in research and removal of outdated and

counterproductive strategies in research, making it a double so renewal: human resources and research strategies.

The proposed theme by this project has already aroused a lively interest in the research teams belonging to universities and prestigious research centers in Romania and in Europe which have already expressed their intention to contribute and collaborate on this project to founding an international thematic networks will aim to tackle the projects under the FP7 frame.

The project is successful in the strategic priorities of the CAPACITIES Program, Module III, Bilateral Cooperation, both by the proposed method and active collaboration with foreign partners, namely University of Hanseo, South Korea. By the objectives and European collaborations started, the theme of interdisciplinary research is important, both scientifically and socio-applied, being appropriate to current research needs.