NATIONAL CENTRE FOR INFORMATION AND DOCUMENTATION

ADVANCES
IN
BULGARIAN SCIENCE

4 2007
SOFIA

Published by National Centre for Information and Documentation
52 A G. M. Dimitrov Blvd
1125 Sofia, Bulgaria,
Phone: +359 2 817 38 62
http: www.nacid.bg,
e-mail: advances@nacid-bg.net

Editorial board:
Kamen Velev
Vanya Grashkina, Olga Racheva,
Yana Panova, Kostadin Tonev,
Milen Angelov, Tzvyatko Stoyanov
Lyudmila Velkova

Disclaimer
The articles are published as provided by their authors, without additional editing.

ISSN: 1312-6164

© National Centre for Information and Documentation 2005 - Publisher
© PrePress by Svetoslav G. Marinov Ltd., Sofia, Bulgaria
© Printing by Milena Print Ltd., Sofia, Bulgaria
© Cover design by Svetoslav G. Marinov Ltd., Sofia, Bulgaria

NATIONAL RESEARCH PROGRAM "NANOTECHNOLOGIES AND NEW MATERIALS"

Nanotechnologies are one of the most modern and in full force developing spheres of science and practice in the whole world. They are based on properties possessed by nanomaterials built from different nanoparticles (domains, crystals, grains, pores, mycels, etc.) with sizes from several to several dozens of nanometers, as well as on new processes used for their processing. At the nanometric level substance is ruled by new laws leading to analogies between molecules and nanoparticles consisting of several hundred to several thousand atoms. Examples of nanoobjects are nanoparticles (semiconductor, metallic and oxidic), nanocrystals, fulerens and carbonic nanotubes, nanopores, quantum dots, threads and holes, thin films, nanocolloids, and a number of other objects having at least one size in the nanometric sphere.

Nanotechnologies are an interdisciplinary sphere combining inorganic and organic chemistry with physics, biology and materials science. In this way they are the latest science-technical revolution, results of which can be seen in all spheres of material production and in everyday life. It is expected that in the XXI century they will change conditions of human life through creation of new and improving the existing products and technologies.

National research program "Nanotechnologies and New Materials" is in conformity with the long-term prognostication for development of economy, science, social and public life in the country and with inclusion of Bulgarian research and production teams into the European Research Area.

Conditions for research in the sphere of nanosized materials traditionally exist in Bulgaria. The activities directly correlate with European research programs and world trends in this field and aim at:

- *Creation of favourable conditions for development of research infrastructure in accordance with international criteria and national interests;*
- *Increase of competitiveness of the research and technological potential of the country and improving the quality of life through stimulation of nanotechnologies and new materials application in the national industry;*
- *Integration of small and medium-size enterprises in research consortia through development of joint projects envisaging transfer of knowledge;*
- *Integration of the Republic of Bulgaria into the European community as an equal and sought partner in the field of development and implementation of nanosized materials, technologies and products.*

Research priorities are as follows: materials science of nanosized materials with multifunctional properties; super-thin layers and multi-layer nanosystems; nanometrology and its application.

The National program puts some basic tasks for solution as under:

- *Development of a mechanism for fostering research investigations in the field of nanotechnologies and new materials;*
- *Stimulation of technological transfer with a view to meeting the demands of the society;*
- *Strengthening of the links "academy – industry";*
- *Creating a stimulating environment for social educational process based on knowledge in the field of nanotechnologies and realization of young specialists – new generation of scientists of the XXI century.*

NACID

National Centre for Information and Documentation

MAIN OBJECTIVES

NACID is a governmental institution affiliated to the Ministry of Education and Science. NACID collects, processes, maintains and disseminates reference and analytical information to support the national policy in the field of education, science and innovation as well as to support Bulgarian research bodies, individual researchers and SMEs

PRIMARY FIELDS OF ACTIVITIES

- Processing and disseminating bibliographic, reference data and analytical information.
- Maintaining specialized databases of scientific production and research resources in Bulgaria.
- Providing information about national, European and trans-European research programs.
- Providing information to support the process of harmonization of the Bulgarian education and research legislation with European Union ones.
- Performing the role of institutional contact point of the Sixth Framework Program in Bulgaria.

INFORMATION PRODUCTS AND SERVICES

- NACID offers a large range of information products, including:
- Subject profiles;
- Reviews;
- Bibliographic references.

- NACID offers a great variety of information services through its own databases as well as information brokerage to external databases. Online access to two information blocks of *locally maintained own databases* in English:

"Bulgarian Science" Databases

- *"SIRENA",* R&D reports and dissertations;
- *"Scientific and Technical Publications in Bulgaria";*
- *"Who is Who in Bulgarian Science" ;*
- *"Papers" ,* Number of Records.

" Science and Industry" Databases

- "*Partnership for Innovation and Development",* Information about the national research units.
- *"Knowledge for Innovations and Development" ,* Information about Bulgarian R&D activities.

The information brokerage services are available upon request, providing access to over 1200 databases from major international commercial host centers, thus providing the research community with a wealth of S&T information.

- *Central Research and Technical Library services*

- Library collections - more than 4 million items/reference books, monographs, serials, dissertations, CD ROM, DVD etc.;
- Online access to the library catalogues since 1980;
- Searching in electronic catalogues and databases;
- Lending of library materials;
- Electronic Document Delivery;
- Interlibrary loan;
- More than 9000 users per year.

CONTENTS

NATIONAL SCIENTIFIC PROGRAMMES WITH EUROPEAN DIMENSIONS

DIRECTED SYNTHESIS AND COMPUTATIONAL MODELING OF FUNCTIONAL ORGANIC COMPOUNDS FOR IMMOBILIZATION IN SOLID MATRIXES

Rositca Nikolova, Ivan Petkov, Georgi Vayssilov, Faculty of Chemistry, University of Sofia
1, James Bourchier Blvd., 1164 Sofia, Bulgaria
E-mails: rnikolova@chem.uni-sofia.bg; ipetkov@chem.uni-sofia.bg; gnv@chem.uni-sofia.bg
Tzonka Mineva, Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, and UMR5253
Institut C. Gerhardt, CNRS, Ecole Normale Superior de Chimie, Montpellier, France
E-mail: tzonka.mineva@enscm.fr

Abstract

The paper describes activities and results of four partner groups working on a joint research project within the National research programs "Nanotechnology and new materials" of the Bulgarian national research fund. The project was directed towards development of composite materials with specific optical and photochemical properties. It combined molecular design of organic components and synthesis of new organic components, suitable for immobilization; quantum chemical analysis of their structure and optical properties; investigation of the spectral and photochemical features of immobilized compounds and compounds in solution.

INTRODUCTION

One of the most efficient ways for exploration of a complex research problem or development of new materials and substances with predefined properties is to combine efforts of different research groups with complementary expertise and common interests. Formation of such extended research teams was stimulated in the past years via the National research programs of the Bulgarian national research fund. Under one of these programs entitled "Nanotechnology and new materials", we worked together towards development of composite materials with specific optical and photochemical properties for application in optics, optoelectronics, optical data storage, etc. Optically active components of a composite are based on organic compounds with defined spectral properties, immobilized in different media – polymers or microporous molecular sieves, in order to provide reliability, efficiency and controlled properties of the composite material. The project combined molecular design of organic components and synthesis of new organic components suitable for immobilization; quantum chemical analysis of their structure and optical properties; investigation of the spectral and photochemical features of immobilized compounds and compounds in solution. The research plan was organized in four subprojects, which are interconnected and include consecutive stages of design, preparation and characterization of the composite materials. A specific subproject is directed towards education and training of specialists at high educational level – masters or PhD, in these fields.

QUANTUM CHEMICAL INVESTIGATIONS

The quantum chemical investigations aimed at clarification of the structure, reaction mechanisms and spectral features of the new organic compounds. In particular, we modeled substituted coumarins containing phosphorus[1,2,3] which were also experimentally synthesized within the project.

In order to clarify the mechanism of a tandem reduction/acylation reaction of the diethyl ester of coumarin-3-phosphonic acid with $NaBH_4$ and acetic anhydride[4] (Fig. 1) we performed computational study at MP2 and B3LYP levels. This reaction is particularly interesting since it experimentally results in formation of C-acylated isomer only, while under similar reaction condition also O-acylated product should be expected. The observed regioselectivity for C-acylation could be explained by the higher stability of C-acylated as compared to O-acylated product both in pyridine and THF, by 54-56 kJ/mol. In addition, important role for the regioselectivity is played by high negative charge on the C3 atom, -0.87 (-0.77) e, in the complex of adduct of hydrogenation with Na^+, H-ad/Na (see Fig. 1 and Fig. 2b), which is actually the species undergoing acylation with acetic anhydride. The important electronic factor is that a p-orbital of C3 atom has dominant contribution, above 70%, into the C2=C3 π-MO, which is by 0.69 eV less stable (i.e. more reactive) than the lone pair orbitals of the alternative reactive center, O9. The later orbitals are stabilized due to participation of O9 atom in the coordination of the Na^+ cation that reduces the nucleophilicity of the O9 electrons and consequently disfavors O-acylation [1].

Additional important feature of this reaction is formation of two types of Lewis acids after the first step of the reaction, sodium or other alkaline cation and BH_3. Our calculations suggested that BH_3 could bind to the nucleophilic centers of the anionic intermediate adduct and thus suppress its further acylation. Such problem is likely the reason for the drastically reduced yield of the acylation product if a strong base is absent in the reaction mixture, as found experimentally [4]. In this direction, both computational results and comparison with experimental observations suggest that a crucial role for a successful acylation is played by dimethylaminopyridine (DMAP), which binds the strong Lewis acid BH_3 generated during the first step of the tandem reaction. If DMAP is not available in the reaction mixture before hydride reduction step, the formed BH_3 binds to the C3 atom of the adduct H-ad and likely suppresses its further acylation [2].

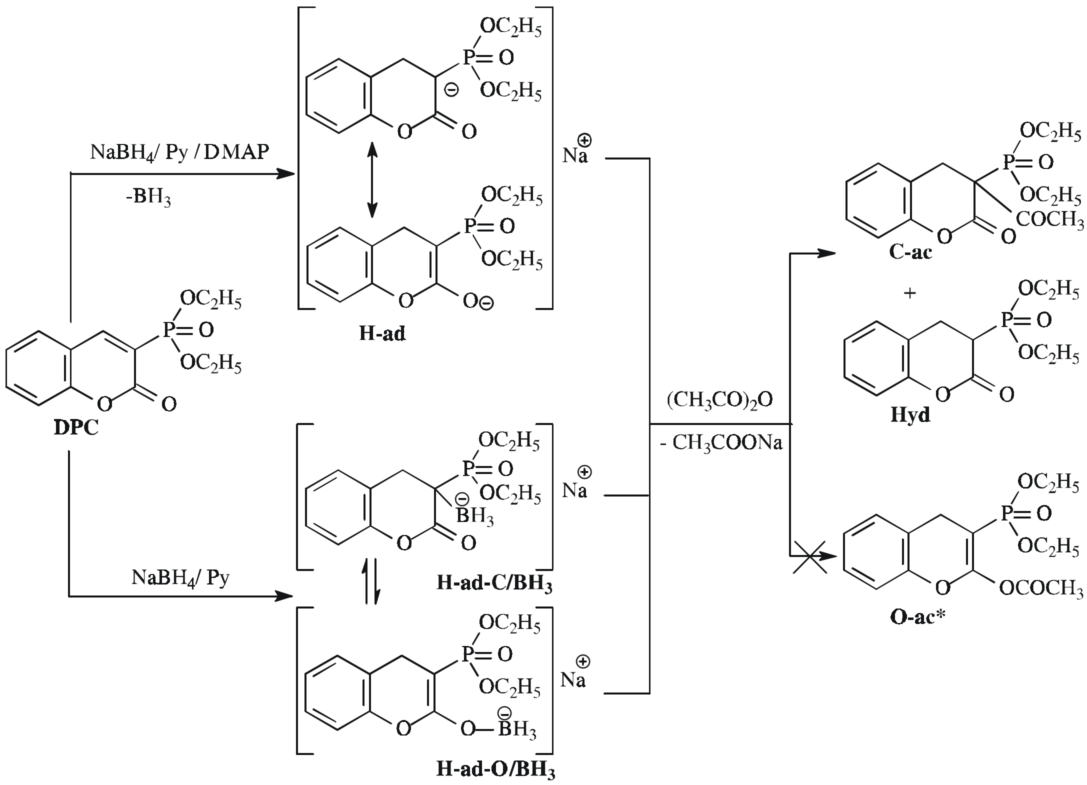


Fig. 1. Reaction scheme for the tandem reduction/acylation reaction of the diethyl ester of coumarin-3-phosphonic acid with $NaBH_4$ and acetic anhydride (* **O–ac** product has not been isolated).

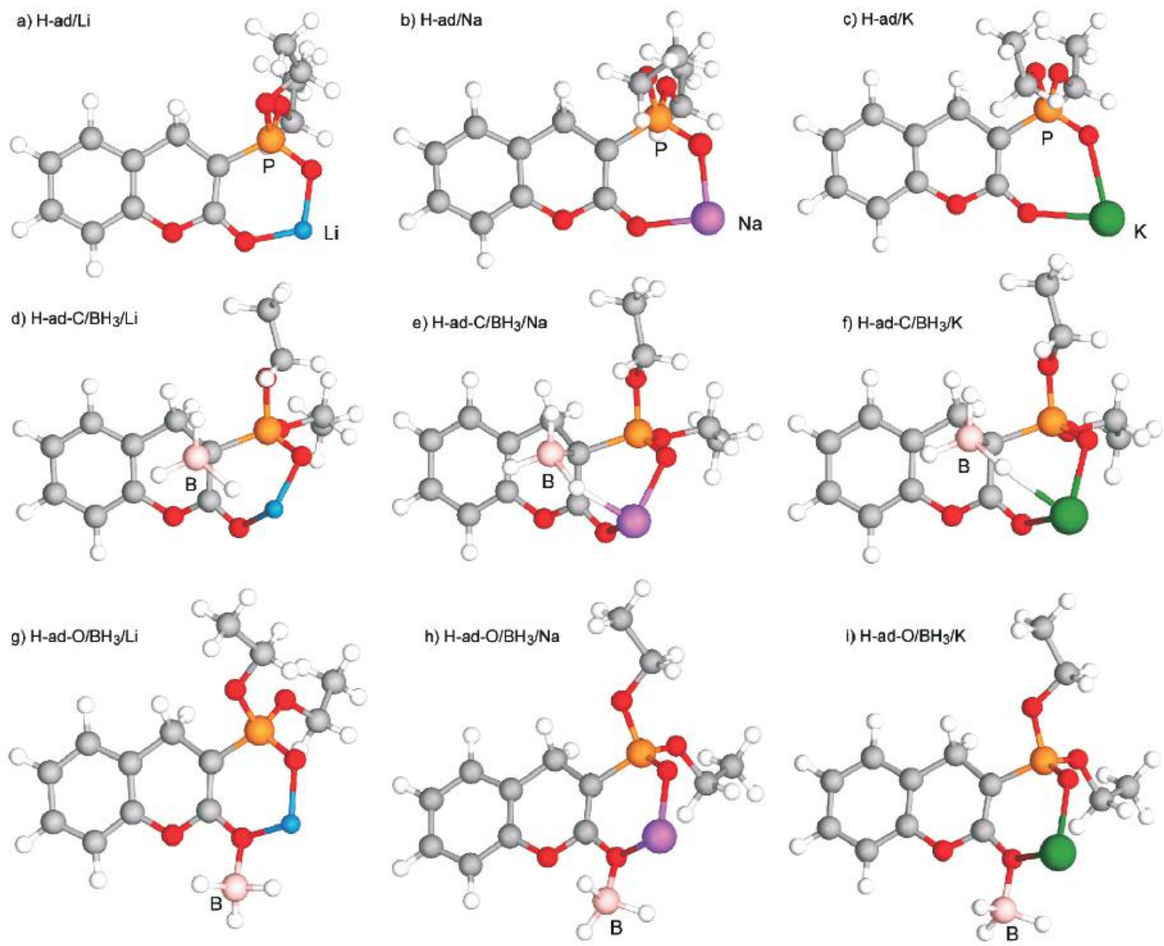


Fig. 2. Optimized structures of various proposed intermediate complexes for the tandem reduction/acylation reaction of the diethyl ester of coumarin-3-phosphonic acid with different alkaline boron hydrides and acetic anhydride.

Table 1. Binding energy (in kJ/mol) of BH_3 in the complexes with the intermediate, solvent molecules and DMAP obtained at MP2/6-311+G*//HF/6-31+G* in gas phase or in solvent.

Complexes with BH_3	Gas phase	Pyridine	THF
THF + BH_3 ⇆ THF.BH_3	-99	-110	-110
Py + BH_3 ⇆ Py.BH_3	-143	-159	-152
DMAP + BH_3 ⇆ DMAP.BH_3	-151	-168	-166
H-ad / Li + BH_3 ⇆ H-ad-C/ BH_3 / Li	-160	-151	-150
H-ad / Li + BH_3 ⇆ H-ad-O/ BH_3 / Li	-127	-104	-104
H-ad / Na + BH_3 ⇆ H-ad-C/ BH_3 / Na	-170	-150	-183
H-ad / Na + BH_3 ⇆ H-ad-O/ BH_3 / Na	-141	-114	-140
H-ad / K + BH_3 ⇆ H-ad-C/ BH_3 / K	-182	-173	-173
H-ad / K + BH_3 ⇆ H-ad-O/ BH_3 / K	-143	-122	-123

In order to clarify the influence of the by-products from reduction with alkaline boron hydride, alkaline cations and BH_3, on subsequent reaction steps in a tandem one-pot reaction we modeled formation of complexes of the ambident anionic intermediate with the alkaline cations and with BH_3 bound to C or O center of the intermediate (Table 1). The relative stability of these complexes in THF or pyridine has been compared to the stability of the complex of BH_3 with DMAP, which is also present in the experimental reaction mixture. For Na^+ and Li^+ as counter cations the complex DMAP.BH_3 in pyridine is more stable than the complexes of BH_3 with the intermediate. In presence of K^+ the complex of BH_3 bound to C atom is more stable than DMAP.BH_3, i.e. even DMAP is not basic enough to bind BH_3 and the intermediate in this case is blocked for further acylation [2]. From this comparison we can conclude that the reaction will proceed faster and with higher yield with $LiBH_4$ compared to $NaBH_4$, while with KBH_4 it will not occur if stronger Lewis base is not added.

We should highlight the importance of the solvent for the reaction, which influences the relative stability of different complexes with BH_3, namely in pyridine BH_3 is bound stronger in DMAP.BH_3 than in H-ad-C/BH_3/Na complex, while in THF the order of stability is the opposite and the acylation is less efficient than in pyridine.

Another computational study [3] is connected with the reaction of α-halogenated ketones with trialkyl phosphates, which proceeds in two directions, leading to the corresponding β–oxophosphonates and vinyl phosphates [5,6]. However, it was reported recently [7] that when 3-(ω-bromoacetyl)coumarin reacts with trialkyl phosphites (Fig. 3) isolated dialkyl vinylphosphates are found to be the only products, whereas the interaction of 3-(ω-bromoacetyl)coumarin with triphenyl phosphite gives only β–oxophosphonate. To understand better whether the thermodynamics or kinetics of the reaction under discussion leads predominantly to the observed regioselectivity of 3-(ω-bromoacetyl)coumarin we have examined the electron density distribution associated with the geometrical structures of the products and atomic reactivity indices of the reagents that were further rationalized in terms of the local hard-soft acid base (HSAB) principle [8].

The geometry of 3-(ω-bromoacetyl)coumarin, trialkyl phosphites, triphenyl phosphite, β–oxophosphonates and vinyl phosphates was optimized with both gradient-corrected (BP86) and hybrid (B3LYP) exchange-correlation functionals. Both isostructures, phosphonate (R = Ph) and phosphates (R = Me, Et), were found to be comparable in their stability. The employed computational methods reproduce well the IR features as suggested from the comparison between the experimentally observed and computed vibrational frequencies [3].

Applying the ARHT (atomically resolved hardness tensor) method to determine atomic Fukui indices and total hardness has shown to be useful in predicting reactivity of the obtained products and to distinguish reactivity of different centers. The reactivity index numbers are helpful also in rationalizing quantitatively the evolution of the active centers from the reagents to the products. Thus, the predicted superior reactivity for diphenyl-1-(2-oxo-2H-chromen-3-yl)-2-vinylphosphate is attributed to the enhanced

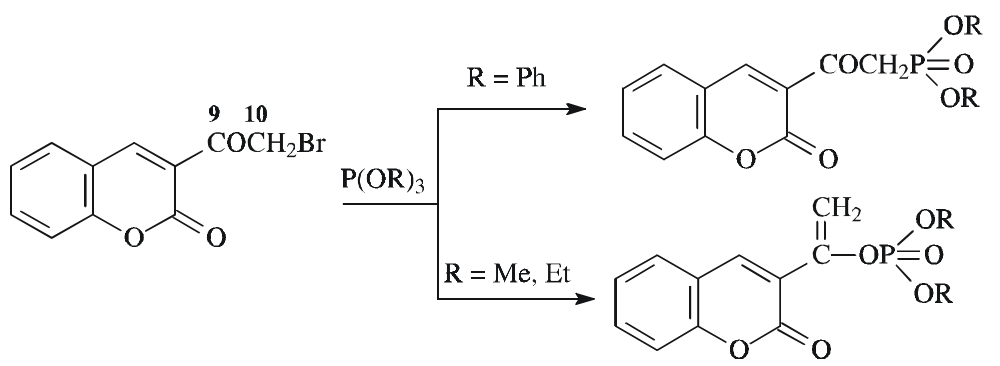


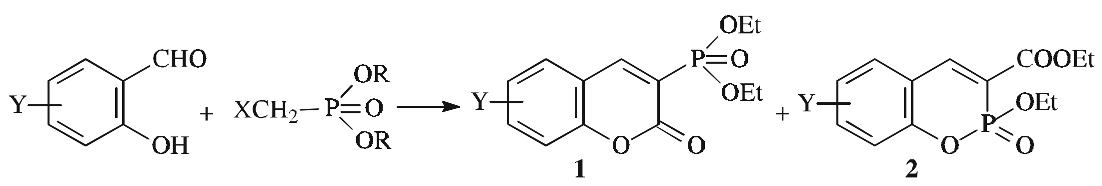
Fig. 3. Reaction scheme for the interaction of 3-(ω-bromoacetyl)coumarin with phosphites

delocalization of the electron density around the phosphorous atom caused by creation of the P-O bond. However, on the basis of the atomic Fukui functions of probable reaction centers in the reagents, it is not possible to distinguish neither between both concurrent C9 and C10 atoms in 3-(ω-bromoacetyl) coumarin, nor between the P centers in the trialkyl phosphites (R = Me, Et) and triphenyl phosphite. Therefore, we can only conclude that electron substitution effects play more significant role for the observed regioselectivity than the hard-soft relations in terms of the local HSAB principle.

SYNTHESIS OF COMPOUNDS WITH FUNCTIONAL PHOSPHOROUS-CONTAINING GROUPS

During the last few decades the interest in synthesis and investigation of different coumarin derivatives and analogues has vastly increased mostly due to specific properties of these compounds and their multidisciplinary application in organic synthesis, agrochemistry, medicine, laser technologies, etc. On one hand, particular interest towards this class of organic compounds is due to their potential application as acceptors in different organic reactions with nucleophilic reagents and dienophiles in Diels-Alder reactions and in reactions of 1,3-dipolar cycloaddition as well as to their application as intermediates in the synthesis of products of practical interest. On the other hand, especially important are their antimicrobial, antiviral, anticancer, enzyme inhibition, anti-HIV, and antioxidant activities as well as their influence over central nervous system [9]. Modern technologies are the third large area of application of coumarin derivatives since coumarins containing specific substituents are applied as excellent luminophores and laser dyes due to their strong absorption cross-section and large radiative yields [10]. The conjugated bonds in these compounds are most probably responsible for electron transitions in the visible or UV region that determines large variety of their photochemical features, thus making coumarin derivatives attractive compounds for various practical purposes [11].

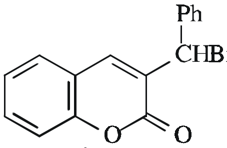
The phosphorus-containing coumarin derivatives synthesized so far are known to exhibit various types of biological activity; they are used in the medicine, as pesticides etc [12]. Specific properties of these compounds are due to the presence of two functional groups in their structure and the unique combination of different characteristics of both groups. Additional feature of most of the phosphorous-containing coumarins, as a combined effect of the carbonyl and phosphonate groups, is the formation of chelate complexes with metal cations, which is particularly important for their application in medicine. Despite numerous publications concerning methods for synthesis and analysis of 3-substituted 2-oxo-2H-1-benzopyrans (coumarins) containing electron-acceptor group, the chemical behavior and properties of phosphorus-containing coumarins are still not very well studied and understood [13, 14, 15]. By this reason in the last years our research efforts have been directed mainly towards synthesis of new phosphorous-containing coumarin derivatives and detailed investigation of their chemical behavior and properties [7, 16, 17]. We developed a synthetic method for preparation of the phosphorus-containing coumarin derivatives **1** and **2** via interaction of salicyl aldehyde with triethylphosphonoacetate under Knoevenagel reaction conditions [16]. In order to establish the influence of the reaction conditions on the regioselectivity of the reaction and the yields of products, the interaction was carried out under various experimental conditions. The regioselectivity of the studied reactions was explained by stereoselectivity in the formation of the possible intermediates in the first step of the reaction.



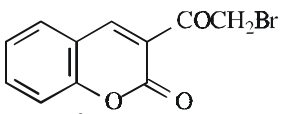
Y = H, 6-Cl, 6-Br, 7-NEt_2 X = $COOCH_3$, $COOC_2H_5$, CN, COOH R = CH_3, C_2H_5

Diethyl 1,2-benzoxaphosphorine-3-carboxylates **2** undergo a regio- and stereoselective [2+2] photodimerization in methanol solution under the action of sunlight giving the corresponding *anti* head-to-tail dimmers [18].

In order to synthesize new class of phosphorous-containing coumarin derivatives we thoroughly investigated the interaction of both the bromine-containing derivative **3** and 3-(ω-bromoacetyl)coumarin **4** with phosphates [7]. Having in mind potential biological activity of the target coumarin derivatives, several compounds of the series **1** and **3** have been tested and most of the representatives were found to possess relatively high activity as growth regulators [19].

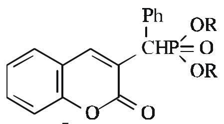


3

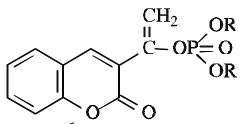


4

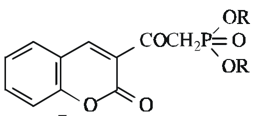
The further synthetic investigations showed that the phosphonates **5** could be obtained from 3-(1-bromobenzyl)-2-oxo-2H-1-benzopyran **3** in Arbuzov reaction conditions as can be predicted, while the interaction of bromoacetylcoumarin **4** with trialkylphosphonoacetate results mainly in the synthesis of enolphosphates **6**. The interaction of the bromine-containing derivative **4** with dialkylphosphites was also studied but instead of the expected 2–oxoalkanephosphonates **7** we obtained and isolated epoxyphosphonates **8**.



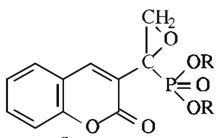
5



6



7



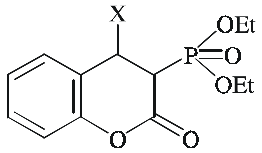
8

On the basis of the studied reactions we developed a novel synthetic method for preparation of phosphonates **7** based on the preliminary blocking of the carbonyl group in the initial bromine-containing derivative and following interaction with phosphites.

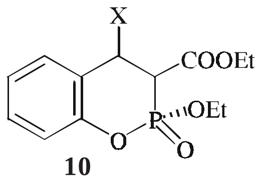
The conjugate addition of phosphites to 3-substituted coumarin derivatives was also investigated and a proficient laboratory method was developed for preparation of 1,4-addition products in the presence of toluensulphonic acid [17]. In this case the use of ultrasound increased the yield of the target compounds 3-acyl-4-diethylphosphono-2-oxochromanes to quantitative.

Investigations on the chemical behavior of the 3-substituted 2-oxo-2H-1-benzopyranes (coumarins) towards nucleophilic reagents exhibit that they are good acceptors in the reaction of 1,4-addition. We expected that phosphorous analogs of coumarin-3-carboxylic acid would have similar properties. In this connection the interaction of diethyl ester of 2-oxo-2H-1-benzopyran-3-phosphonic acid with organometallic reagents was studied.

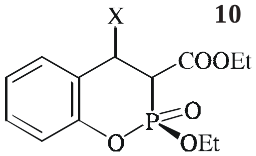
When the reactions of the coumarin **1** were carried out with organomagnesium, organozinc, or Ivanov's reagent, 2-oxochromanes **9** were isolated with good yields. The reactions with 1,2-benzoxaphosphorine **2** as substrate had the same synthetic progress but in these cases only two of possible diastereoisomers were isolated.



9



10

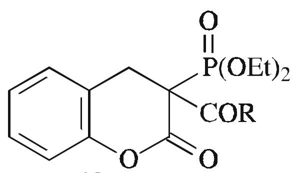


11

X = Et, Pr, *i*-Pr, CH_2Ph, CH_2COOH, RCHCOOEt, PhCHCOOH, $CH_2COOC(CH_3)_3$

The reactions were also carried out under ultrasound action and in these cases the yields of the target products were higher and the results were precisely reproduced.

We have also been interested in the interaction of the 3-phosphonocoumarin **1** with various anhydrides in tandem one-pot reactions of hydride reduction/acylation. Optimization of the reaction conditions resulted in preparation of C-acylation products **12** with high yields [4].



12

R = Me, Et, Pr, *i*-Pr

SPECTRAL STUDIES AND PHOTOCHEMICAL BEHAVIOR OF IMMOBILIZED SPECIES

The preparation of the immobilized photosensitive organic compounds will be described on the example of two types of dye molecules in cyclodextrins (CD) [20-22]. Cyclodextrins are cyclic oligosaccharides with six to eight glucose monomers in a ring. Since each of the chiral glucose rings is in conformation chair, the whole macrocycle forms an empty cone. Due to the presence of OH groups on one side of the cyclodextrin's cone, it is hydrophobic inside and hydrophilic outside. This specific feature of cyclodextrins allows formation of various host-guest complexes (Fig. 4) with hydrophobic molecules in water solution.

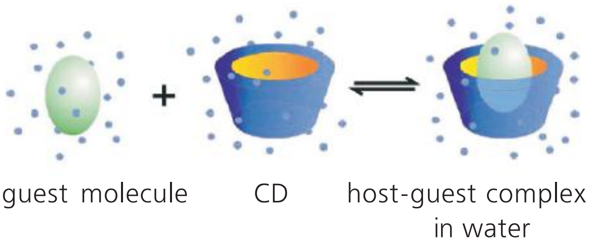


Fig. 4. Schematic representation of formation of host-guest complexes of hydrophobic molecules with cyclodextrin

The investigation concerned inclusion of two dye molecules, 4-dimethylamino-4'-methoxy-azobenzene [20,21] and 3-(4-dimethylaminophenyl)-2-benzothiazol-acrylonitrile [22] in β-CD. The complexes were prepared by two approaches:

i. Sorption from mixed solvent: $CH_3CN:H_2O=2:1$ and $DMSO:H_2O=5:1$.

ii. Preparation of separate solutions of β-CD in water and of dye in organic solvent (methanol), followed by mixing of the two solutions and heating. After that, cooling of the mixture at 0°C resulted in formation of a crystal product soluble in different organic solvents.

The changes in the absorption spectra of the samples produced with the azo-dye by the first method (with $CH_3CN:H_2O$) with irradiation time are shown in Fig. 5. The spectra of the free azo-dye in absence of β-CD are also shown. Similarly to the other azo-dyes, 4-dimethylamino-4'-methoxy-azobenzene, which we used, exists in two isomeric forms with respect to the central N=N bond, cis and trans, and the latter form is more stable. The absorption spectrum of the azo-dye shows a large peak at 413 nm and a less intensive one at 316 nm. After UV-vis irradiation of the free dye molecules in solution (left panel of Fig. 5), a photoisomerisation of the trans into cis isomer takes place, which is accompanied by appearance of a maximum at 377 nm, characteristic for the cis form. After long irradiation the maxima at 413 and 316 nm disappear, which is an indication for complete transformation of the trans into cis isomer. Such photoisomerisation occurs also in presence of β-CD (right panel of Fig. 5), however, after the same irradiation time large amount of trans isomer is still observed in the sample. This is an indication that part of azobenzene molecules form a stable complex inside the β-CD cavity and remain unaffected by the irradiation [20].

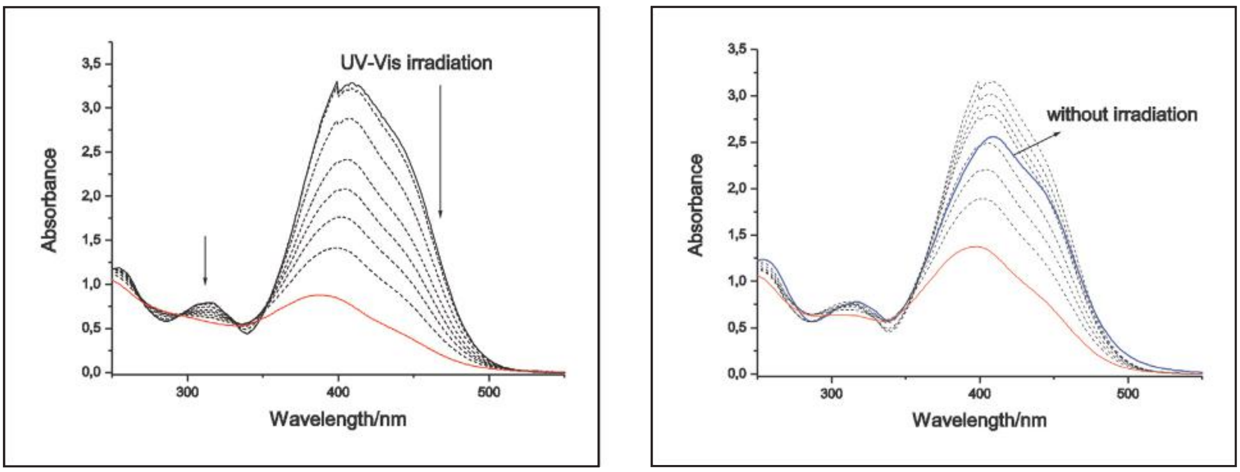


Fig. 5. Changes in the UV-vis spectra of the azo-dye obtained after irradiation with UV-vis light in presence (right panel) and absence (left panel) of β-CD

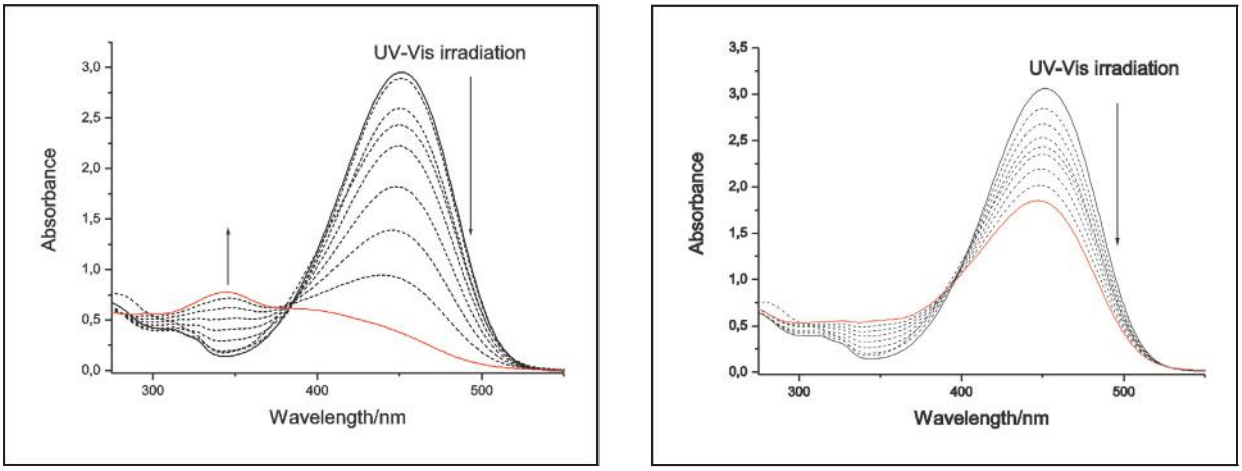


Fig. 6. Changes in the UV-vis spectra of the benzothiazol-dye obtained after irradiation with UV-vis light in presence (right panel) and absence (left panel) of β-CD

Similar results have been observed also for the benzothiazol dye (Fig. 6) [22]. The free benzothiazol molecules in solution absorb at 450 nm, while after the irradiation this absorption band decreases and a new band with maximum at 346 nm appears. This transformation is again an indication for photoisomerisation of trans to cis form of the dye molecule with respect to the central double carbon-carbon bond. The influence of the β-CD (right panel of Fig. 6) in this case is more pronounced than in the complex with the azo-dye. For the same irradiation time the absorption maximum characteristic for the trans form slightly decreases but even at large irradiation times considerable part of the benzothiazol molecules remain in trans form. This is an indication that the complex of the benzothiazol molecules with β-CD prevents isomerisation of trans to cis form.

As mentioned above, the second approach for inclusion of the dye molecules in β-CD resulted in formation of crystals which were subsequently investigated in different solvents. An example of spectral changes for the complex of azo-dye with β-CD after irradiation with UV-vis light in THF is shown in Fig. 7. It is clearly seen that the presence of the β-CD again does not allow complete photoisomerisation of the dye from trans to cis form. From the analysis of the spectra and the dependence of the photoisomerisation on the concentration of the studied solutions one can deduce that the stoichiometry of the complex is not 1:1 but includes more than one dye molecule.

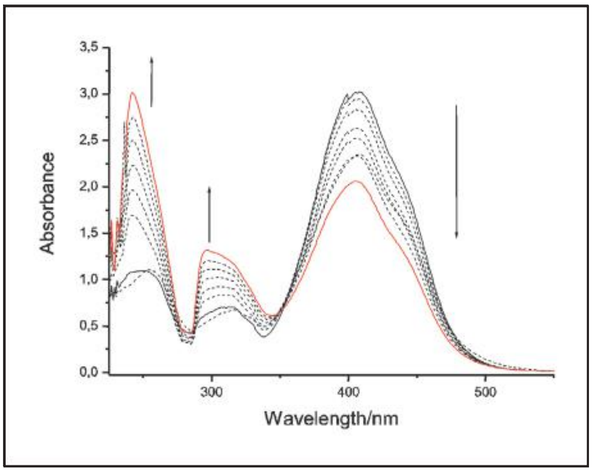


Fig. 7. Changes in the UV-vis spectra of the complex of azo-dye with β-CD after irradiation with UV-vis light in THF

References:

1. Petkova N. I., Vayssilov G. N., Nikolova R. D., Bojilova A. G. J. Mol. Struct. THEOCHEM 759, 177 (2006).

2. Petkova N. I., Nikolova R. D., Bojilova A. G., Vayssilov G. N. Int. J. Quant. Chem. 107, 1814 (2007).

3. Nathaniel R., Mineva T., Nikolova R., Bojilova A. Int. J. Quant. Chem. 106, 1357 (2006).

4. Petkova N. I., Nikolova R. D., Bojilova A. G., Rodios N. A., Raptopoulou C. P. Synth. Commun. 36, 509 (2006).

5. Lichtenhalter F. W. Chem. Rev. 61, 607 (1961).

6. Borowitz I. J., Anshel M., Firtenberg S. J. Org. Chem. 54, 1723 (1967).

7. Nikolova R., Bojilova A., Rodios N. Tetrahedron 54, 14407 (1998).

8. Pearson R. G. J. Am. Chem. Soc. 85, 3533 (1963).

9. Borges F., Roleira F., Milhazes N., Santana L., Uriarte E. Curr. Med. Chem. 12, 887 (2005).

10. Schäfer F. P. Dye Lasers, 3rd ed.; Springer-Verlag: Berlin, New York, 1990; Vol. 1, p. 244.

11. Cave R. J., Burke K., Castner E. W. Jr. J. Phys. Chem. A 106, 9294 (2002).

12. Budzisz E. Phosphor, Sulfur, Silicon 179, 2131 (2004).

13. Li X., Wang Y., Fu H., Jiang Y., Zhao Y. Bioorg. Chem. 34, 105 (2006).

14. Takeuchi Y., Ueda N., Uesugi K., Abe H., Nishioka H., Harayama T. Heterocycles 59, 217 (2003).

15. Petrov P. J., Alexiev A. A., Petrov G., Giorgi G. J. Heterocyclic Chem. 42, 313 (2005).

16. Bojilova A., Nikolova R., Ivanov C., Rodios N. A., Terzis A., Raptopoulou C. P. Tetrahedron 52, 12597 (1996).

17. Nikolova R. D., Bojilova A. G., Rodios N. A. Tetrahedron 60, 10335 (2004).

18. Nikolova R. D., Vayssilov G. N., Rodios N., Bojilova A. Molecules 7, 420 (2002).

19. Alexieva V., Karanov E., Nikolova R., Bojilova A. Bulg. J. Plant Physiol. 21, 45 (1995).

20. Petinova A., Metsov S., Petkov I., Stoyanov S. J. Inclusion Phenom. Macrocyc. Chem., accepted (2007).

21. Petinova A., Stojanov S., Petkov I., Stojanov S. Cent. Eur. J. Chem., accepted (2007).

22. Petinova A., Stojanov St., Mezov St., Petkov I. J. Inclusion Phenom. Macrocyc. Chem., accepted (2007).

MULTILAYER STRUCTURES AND NANOCOMPOSITES FOR ELECTRONIC APPLICATIONS

Diana Nesheva, Institute of Solid State Physics, Bulgarian Academy of Sciences
72, Tzarigradsko chaussee Blvd, 1784 Sofia, Bulgaria

Abstract

A current project on development and characterization of new nanostructured materials, applicable in several areas of electronics is briefly introduced. The project is realized by combining the experience of three partner teams from Bulgarian Academy of Sciences and Sofia University St. Kliment Ohridski. The activities of the project include: a) fabrication and characterization of multilayer structures with silicon nanoparticles; b) fabrication and characterization of nanocomposites containing nanoparticles of SiO_2 or smectics; c) investigation of the electron structure of GaAs/AlGaAs quantum wires; d) modelling of some material and structural propperties. As an example of the project activities, some recent results on fabrication and characterization of metal-insulator-silicon (MIS) structures with silicon nanoparticles for non-volatile memory applications are described.

INTRODUCTION

Nanocomposites are among the groups of nanomaterial, which have already found and, also, have many potential applications in various life areas such as electronics, optics, optoelectronics, solar energy conversion, medicine, etc. Nanocomposites consist of one or more nanosized phases (fillers) embedded in a matrix as most often they are two-phase systems in which the matrix is an insulating organic or inorganic material and the filler is metal, semiconductor or isolating nanoparticles having size of 1-100 nm.

In materials developed for electronic purposes, in particular composites, the transport of charged carrier is very important. In case the filler concentration is high, above the so called 'percolation threshold', some of the nanoparticles are in contact and form two- or three-dimensional networks. The percolation threshold depends on the material properties of the filler, nanoparticle size and size distribution as well as on the way of incorporation of nanoparticles in the matrix [1, 2]. Therefore, detailed investigations of the effect of preparation conditions on the carrier transport and defect states must be carried out on each new composite material aimed for application in electronics.

When filler concentration is below the 'percolation threshold', current transport can be realized via tunneling of carriers through the potential barriers between nanoparticles. In composites containing microparticles the tunnel current is independent on the temperature, while in nanocomposites it has been observed that their conductivity depends on the temperature. The thermal activation is necessary to ensure carrier transfer from a nanoparticle to another one, when the second nanoparticle is electrostatically charged [3]. The charging effect in nanostructured composites containing single nanoparticles is a fundamental phenomenon. It gives basis of intensive investigations carried out nowadays and directed to development and fabrication of electronic memories using semiconductor nanocrystals [4]. The new memory elements developed recently [5 and reference therein] possess several advantages to those which are in production now, using the floating gate. These advantages include short writing times at low applied fields, long charge storage times at very low leakage currents. Also, practically there is no aging due to the lack of 'hot' carriers. Despite of considerable progress in this direction, further investigations are necessary for optimization of the operation parameters of nanocrystalline electronic memories.

For nanoelectronic materials used in production of corpuses or in capsulation of electronic elements many other properties – thermal, mechanical, dielectric, etc. are very important in addition to the electrical ones [6]. For example, combinations of two nanofillers with different properties and a matrix with good mechanical properties can result in development of many new composites having improved properties [7, 8]. In order to optimize the aggregation process, which is of great importance for the fabrication of nanocomposites, one should develop specific technical procedures for each composite material. Rheological measurements on nanodispersive media and molecular dynamics of nanocomposites can be applied to control the structure of such materials [9]. There are many open problems in the techniques for preparation of nanocomposites, in particular polymer nanocomposites. For example, it is necessary to clarify the relation 'technology-structure-properties', i.e. the relation between the composite structure and preparation conditions as well as to find new kind of fillers, which could make possible fabrication of composites with new, desired properties [9] .

The size reduction of physical objects makes possible to reveal the quantum nature of the matter. Electronic properties of single quantum wells, superlattices, quantum wires and quantum dots have attracted much attention during the last two decades since carrier confinement results in reduction of the electronic density of states, increase of the exciton binding strength, etc. [10]. All these changes lead to new properties of nanosized materials making them interesting from both fundamental and practical points of view. Crystalline semiconductor multilayer structures based on the GaAs/AlGaAs heterojunction and having thickness of individual layers of <100 nm, have already been applied for fabrication of a number of modern electronic and optoelectronic devices.

The project *Multilayer Structures and Nanocomposites for Electronic Applications* is funded by the Bulgarian Ministry of Education and Science in the framework of the National Scientific Programme „Nanotechnologies and New Materials". It aims development of new nanostructured materials suitable for various applications in electronics, and a detailed investigation of their electronic, electrical, rheological, mechanical and dielectric properties. The combination of the long-time experience of the three teams involved in the project in the fabrication and characterization of nanocomposites and multilayer structures results in a successful collaborative work on the following subjects:

A. Formation of silicon nanoparticles in ultra thin SiO_x films with suitable size and spatial distribution of nanoparticles that allow observation of charge effects. The Si-SiO_x films are included in multilayer structures suitable for preparation of electronic memories. The work in this direction is carried out in the Division of Nanophysics, Institute of Solid State Physics, Bulgarian Academy of Sciences.

B. Synthesis of thermo-reactive nanocomposites with new mechanical, electrical and dielectric properties based on epoxy and polyester resins with nanosized fillers embedded. The new composites are an alternative of materials used in contemporary electronics. The work in this direction is carried out in the Formation of Composites Department, Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences.

C. Investigations of electronic properties of GaAs/AlGaAs quantum wires by means of photoconductive spectroscopy. The work in this direction is carried out in the Department of Condensed Matter Physics, Faculty of Physics, Sofia University St. Kliment Ohridski.

MATERIALS PREPARATION AND CHARACTERIZATION

Various techniques such as ion implantation of Si in SiO_2, simultaneous sputtering of Si and SiO_2, sputtering of Si in oxygen, plasma and laser-assisted decomposition of silane, thermal evaporation, etc. are used for preparation of SiO_x ($x \leq 2$) layers that serve as a basic ingredient in the memories with nanoparticles. Among the most harmless, widely known and comparatively inexpensive techniques are the simultaneous sputtering of Si and SiO_2 and the thermal evaporation of silicon monoxide in vacuum or oxygen surrounding. It is important that the thermal evaporation of SiO is fully compatible with the modern Si technology. This is the technique we use for deposition of SiO_x layers with controlled composition and thickness. Amorphous or crystalline Si nanoparticles are formed by annealing in an inert atmosphere at various temperatures and times [11-13].

Fig. 1 shows a cross-section micrograph of a SiO_x layer annealed at 1000°C for 60 min in nitrogen. The micrograph reveals nanocrystals of spherical or oval shape and proves the growth of Si nanocrystals upon such annealing.

The high resolution electron microscopy data did not show crystalline silicon phase in films annealed at 700°C but Raman scattering measurements performed have indicated formation of amorphous silicon phase (see Fig. 2).

It is well known that bulk crystalline Si does not show photoluminescence at room temperature. However, the reduction of its size to dimensions less than 5 nm results in visible light emission from both crystalline and amorphous nanoparticles. The photoluminescence colour depends on the nanoparticle size and structure. We observed quite intense luminescence from films containing crystalline or amorphous pure Si phase [12, 14]. The latter indicates that the annealing at 700°C forms nanosized amorphous silicon particles.

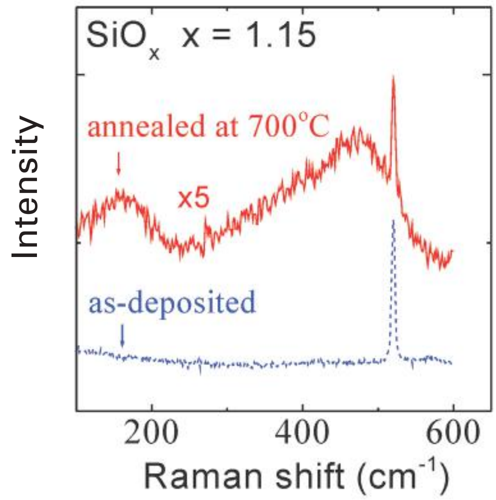


Fig. 2. Raman scattering spectra of a SiO_x film on a crystalline silicon substrate with initial x=1.15 in as-deposited state and after annealing at 700°C for 60 min. Two new wide bands appear in the spectrum after annealing which are typical for amorphous silicon and indicate formation of pure amorphous silicon phase.

The second kind of the project activity regards synthesis of polymer nanocomposites, which is carried out using technologies based on chemical modification of the interphase surface, described in a number of publications [15-17]. New techniques for orientation and/or disper-

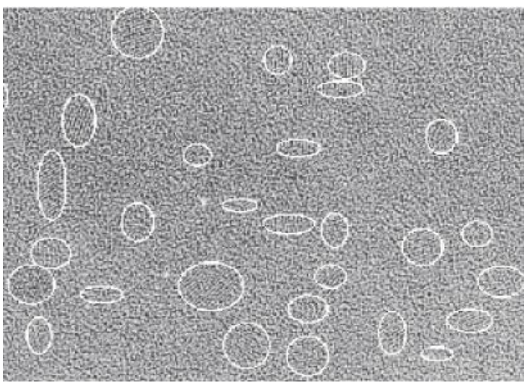


Fig. 1. Cross-section micrograph of a SiO_x layer (x=1.15) obtained by high resolutio electron microscopy. The sample was annealed at 1000°C for 60 min in nitrogen. The white circles mark areas corresponding to crystalline silicon nanoparticles having diameter between 2 and 6 nm.

sion of liquid nanodispersions are under development to control the interactions both between the particles of the filler and between the polymer and the filler. For example, an application of magnetic field is used to the liquid systems to modify locally the distribution of freely dispersed inclusions. The group of methods for investigation of these nanocomposites includes: experimental rheology (established flow and oscillations of the cut), rheological modeling (rheological functions depending on the volume filling, relaxation spectra), structure and morphology of the solid nanocomposites visualized by scanning electron microscopy. The effect of both the nanofillings (carbon nanotubes or aluminum oxide nanoparticles) and the technological processes on the properties of nanocomposites is explored by determination of thermal properties, thermal stability and mechanical properties (deformation and robustness in the regime of bending and impact).

Information on the electrical properties of the polymer composite and Si-SiO_x layers, defect states and charge processes are studied by measuring temperature dependences of dark conductivity, current-voltage and voltage-capacitance (C-V) characteristics at various temperatures and frequencies of the applied electrical field in combination with studies of their structural and dielectric properties.

For investigations on GaAs/AlGaAs quantum wires photoluminescence spectroscopy is most frequently used, since this technique does not require electrical contacts. It has been shown recently that photoconductivity measurements can also give valuable and precise information about optical absorption of nanoobjects [18]. Its application to nanostructured materials is quite important since in these materials the total volume of the nanosized material is normally rather small. The photo-conductivity technique allows direct investigations of both excitons and photocurrent transport in nanosized photoconductors. Therefore, it is applied to explore GaAs/AlGaAs quantum wires. [19, 20].

Computer modeling of the dielectric properties and conductivity of two-phase composite materials has been started. It makes possible to achieve a more reliable interpretation of the experimental results from the infra red transmission spectroscopy on composite films and the studies on voltage-capacitance characteristics of the multilayer structures.

MIS STRUCTURES SUITABLE FOR ON–VOLATILE MEMORIES

An example of the achievements in the project is the preparation of MIS structures for memory applications. Several kinds of structures have been prepared and investigated. The structures are deposited on both p- or n-Si substrates. They contain or not ultra thin (tunnel) SiO_2 layer deposited on the substrate as well as a SiO_x layer and a thin SiO_2 (control) layer between the SiO_x layer and the gate electrode [21-23]. The structures were annealed at 700 or 1000°C to grow Si nanoparticles in the SiO_x layers. Schematic cross-section of experimental structures is depicted in Fig. 3.

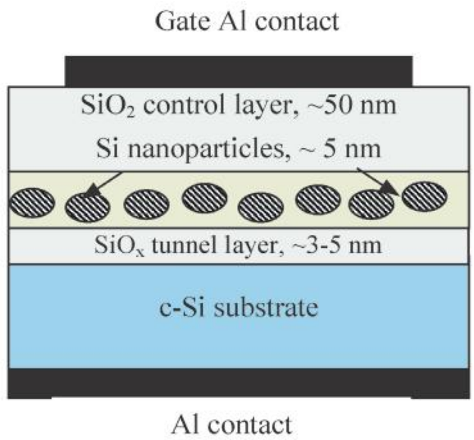


Fig. 3. Schematic cross-section of the experimental MIS structures. The approximate thickness of both SiO_2 layers and Si nanocrystal diameter is given in the figure. The thickness of the layer containing Si nanoparticles is ~15 nm.

Fig. 4 shows normalized C-V curves of a MIS structure on n-Si substrate annealed at 1000°C for 60 min measured in the ranges ±12 V and ±15 V. A clockwise hysteresis is observed, which has been explained [21-23] by charging of the nanocrystals with electrons/holes, which tunnel from the substrate through the thin oxide at positive/negative biases.

In Fig. 5, the retention characteristics of a sample containing Si nanocrystals are shown after charging with +12 or -12 V. The value of the flat-band voltage has been measured during a time interval of about 24 h and used to obtain the flat-band voltage shifts, ΔV_{FB}. It is seen that the charge loss approximately follows an exponential law as the sample loses about 50 % of the trapped charge after 24 hours when charged with a positive voltage. Longer retention times have been measured for samples containing amorphous nanoparticles.

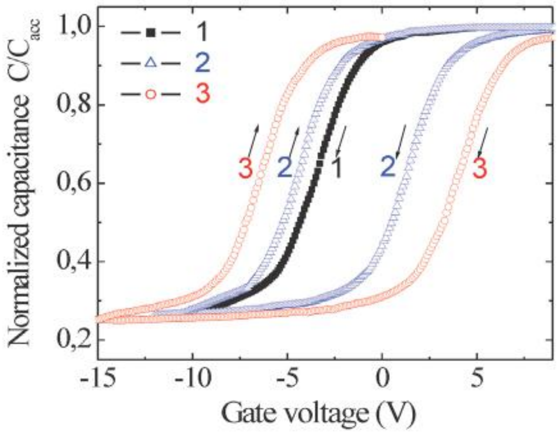


Fig. 4. Normalized high frequency C-V hysteresis curves measured at 100 kHz for samples annealed at 1000°C for 60 min. The scan ranges are ±12 V (curve 2) and ±15 V (curve 3). The initially measured curve is denoted as curve 1. The voltage sweep rate was 0.2 V/s and C_{acc} is the capacitance of the structure in accumulation.

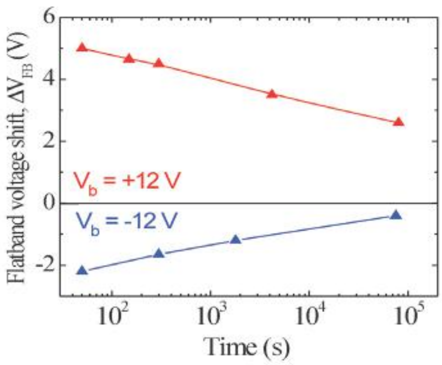


Fig. 5. Charge retention characteristics of a MIS structure annealed at 1000°C for 60 min after charging the nanocrystals with V_b of +12 or -12 V.

CONCLUSIONS

The results received up to now by the teams involved in the project give basis to expect that until closing this project information clarifying the nature of the defects affecting the charge processes in Si-SiO_x nanostructured layers will be obtained. The parameters of the prepared multilayer structures including Si nanoparticles will be optimized regarding their employment as electronic memories. An assessment will be made of the assets and drawbacks from the employment of amorphous and crystalline Si nanoparticles for production of memories.

New polymer nanocomposite materials will be prepared, with good mechanical properties, enhanced thermal stability and controlled physical properties, for application in electronics (for details, adhesives, composite layers etc.). New technological regimes will be developed for dispersion and/or orientation of nanoparticles in polymer matrix, which will allow to control the structure and to improve the properties of nanocomposites.

Information clarifying the electron structure and the nature of optical transitions in GaAs/AlGaAs quantum wires will be obtained.

References:

1. Bera S.K., Chaudhuri S., Gupta R.P., Pal A.K. (2001). Electrical transport studies in nanocrystalline CdSe_SiO2 composite films, Thin Solid Films, 382, 86-94.

2. Lux F. (1993). Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials J. Mater. Sci. 28, 285-301.

3. Sheng P. and Klafter J. (1983). Hopping conductivity in granular disordered systems, Phys. Rev. B 27, 2583-2586.

4. Grabert H. and Devoret M. (1992). Single Charge Tunneling, Plenum, New York.

5. Nesheva D. (2006). Carrier Transport and Gap States in Semiconductor Nanostructures,in Handbook of Semiconductor Nanostructures and Devices, Edited by A.A. Balandin, American Scientific Publishers, volume 1, Chapter 10, pages 453-497 and reference therein.

6. Flandin L., Prasse T., Schueler R., Dchulte K, Bauhofer W. and Cavaille Y.J. (1999). Anomalous percolation transition in carbon-black-epoxy composite materials, Physical Review B, 59, 14349.

7. Vaia R., Krishnamoorti R. (Eds.) (2001). Polymer Nanocomposites: ACS Symposium Series, 804, 39.

8. Hofmann H., Rahmann, Zakia, Ulrich S. (Eds.) (2002) Nanostructured Materials, vol. VIII, p.193.

9. Krishnamoorti R., Giannelis E. (1997). Rheology of End-Tethered Polymer Layered Silicate Nanocomposites Macromolecules, 30, 4097-4102.

10. Wolf E.L. (2006). Nanophysics and Nanotechnology, An introduction to Modern Concepts in Nanoscience, WILEY-VCH GmbH&coGaA, Weinheim,

11. Nesheva D., Bineva I., Levi Z.,. Aneva Z, Merdzhanova Ts. and Pivin J.C. (2003). Composition, structure and annealing-induced phase separation in SiO_x films produced by thermal evaporation of SiO in vacuum. Vacuum, 68, 1-9.

12. Nesheva D., Raptis C., Perakis A., Bineva I., Aneva Z., Levi Z., Alexandrova S., Hofmeister H. (2002). Raman scattering and photoluminescence from Si nanoparticles in annealed SiO_x thin films, J. Appl. Phys, 92, 4678-4683.

13. Bineva I., Nesheva D., Aneva Z., Levi Z., Raptis C., Hofmeister H., Stavrev S. (2003). Effects of annealing atmosphere and substrate on the photoluminescence and Raman scattering from Si nanocrystals in SiO_2 matrix, J. Material Sci.: Materials for Electronics, 14, 799-780.

14. Bineva I., Nesheva D., Aneva Z., Levi Z. (2007). Room temperature photo-luminescence from amorphous silicon nanoparticles in SiO_x thin films, J. Luminescence, 126, 497-502.

15. Kotsilkova R., Fragiadakis D., Pissis P. (2005). Reinforcement effect of carbon nanofiller in epoxy resin system: Rheology, Molecular Dynamics and Mechanical Studies, J. Polym. Sci. Polym. Physics, Part B, 43, 249-258.

16. Kanapitsas A., Pissis P., Kotsilkova R. (2002). Dielectric studies of molecular mobility and phase morphology in polymer-layered silicate nano-composites, J. Non-Crystal Solids, 305, 204-211.

17. Kotsilkova R., Nesheva D., Nedkov I., Krusteva E., Stavrev S. (2004). A study on the rheological and physical properties of carbon/polymer nano-composites. Appl. Polymer, 92, 615-624.

18. Chan C.H., Chen H.S., Kao, C.W., Hsu H.P., Huang, Y.S., Wang J.S. (2006). Surface photovoltage spectroscopy and photoluminescence study of vertically coupled self-assembled InAs/GaAs quantum dot structures, J. Appl. Phys., 100, 064301-6.

19. Donchev V., Kirilov K., Ivanov Ts., Germanova K. (2006). Surface photovoltage phase spectroscopy – a handy tool for characterization of bulk semiconductors and nanostructures, Mat. Sci. Eng. B, 129, 186-192.

20. Donchev V., Ivanov Ts., Wang Y., Djie H.S. and Ooi B.S. (2007). Surface photovoltage spectroscopy of interdiffused InAs/InGaAsAlAs quantum dots, Physica Status Solidi (c), 4, No. 2, pp. 412-414.

21. Nesheva D., Nedev N., Manolov E. and Bineva I. (2007). Memory effect in MIS structures with amorphous silicon nanoparticles embedded in ultra thin SiO_x matrix, J. Phys. Chem. Sol., 68, 725-728

22. Nedev N., Nesheva D., Manolov, E. Bruggemann, R. Meier S., Kirilov K. and Levi Z., (2007). Influence of thermal annealing on the memory effect in MIS structures containing crystalline Si nanoparticles, Journal of Optoelectronics and Advanced Materials, 9, 182-185.

23. Nedev N., Stoytcheva M., Nesheva D., Manolov E., Brьggemann R., Meier S., Levi Z., Zlatev R., Valdez B. and Alvarez L., (2007). MOS Structures Containing Amorphous Silicon Nanoparticles for Application in Memory Devices, NSTI-Nanotech, www.nsti.org, ISBN 1420063766 Vol. 4, p. 485.

THE MONTE CARLO GROUP RESEARCH AND INTERNATIONAL ACTIVITIES IN NANOSCIENCE

Ana Proykova, Head, Computational Theoretical Physics Group, Sofia University, Faculty of Physics
5, James Boucher Blvd., 1164 Sofia, Bulgaria
E-mail: anap@phys.uni-sofia.bg, Web site: http://cluster.phys.uni-sofia.bg

Abstract

Nanotechnology is a crucial field for future scientific development where many different disciplines meet. Computational simulation of nanometer-sized structures is a key issue in this development because (i) it allows a considerable saving of resources and costly experimental setups intended to fabricate nanometric test devices, (ii) nowadays the study of nanometric sized systems is feasible with thoroughly designed computational codes and relatively low cost computational resources, and (iii) it helps in transferring the knowledge from the fundamental science to industrial applications. This article reviews some recent results obtained in the laboratory 'Modeling of physical processes' at the Faculty of Physics, Sofia University. The main objective of our work is to study the interactions at the nano-scale through various computational methodologies in order to get insight into the nature of self-assembly or induced assembly of atoms forming complex objects. The combination of techniques such as classical Molecular Dynamics, special Monte Carlo methods, ab-initio calculations, and density functional theory in a complementary way allows bridging the length and time scales in the important area of nanocluster self-assembly.

INTRODUCTION

Physics is different at the nanometer scale. '*Nano*' is from the Greek 'nanos' (Latin 'nanus') meaning 'dwarf' and denotes 10^{-9}. Properties not seen at a macroscopic scale now become important, such as quantum mechanical and non-equilibrium thermodynamic properties. Rather than working with bulk materials, one works with individual atoms and molecules. By learning about an individual molecule's properties, we can put them together in very well-defined ways to produce new materials with new and amazing characteristics. The invention of new experimental tools as the Atomic Force Microscope (AFM), Scanning Tunneling Microscope (STM), Scanning Probe Microscope (SPM) makes it possible not only to 'see' atoms but to study the dynamics of their ordering and the manner they form complex structures. Currently, there is a large number of complementary instruments that help a scientist in the nano realm.

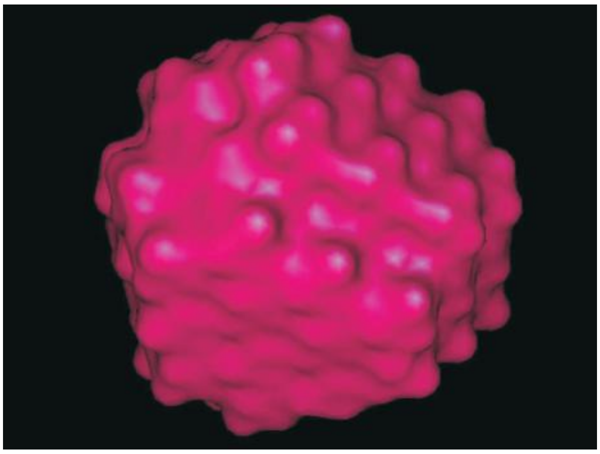
In addition to the enabling technologies, scientists have realized the future potentials of this research based on the fundamental understanding of matter. Laboratories throughout the world are rapidly gaining atomically precise control over matter. As this control extends to an ever wider variety of materials, processes and devices, opportunities for applications relevant to future molecular nanotechnology, defined as the thorough three-dimensional structural control of materials will be created.

Computer applications, launch vehicle improvements, and active materials appear to be of particular interest. With the availability of powerful computers numerical simulations have become a widespread tool to develop a basic understanding of many particle systems and to obtain values for a variety of macroscopic quantities. The most important simulation methods are Monte Carlo (MC) [1,2], Molecular Dynamics (MD) [3], and the Density Functional Theory (DFT) [4]. Each method, if used separately, provides limited information about the system studied under specific requirements. How these methods should be implemented for answering questions about nanosystems has been the core of the article published in the book 'Nanoscale Magnetic Oxides & Bio-World', [5].

GOALS OF RESEARCH

The scientific research in my group (Monte Carlo Group, http://cluster.phys.uni-sofia.bg/) is in the field of computational theoretical physics. We apply simulation techniques (Monte Carlo, Molecular Dynamics and Genetic Algorithm) and heavy quantum calculations (DFT and ab-initio) to study various **properties of nanoscaled systems**:

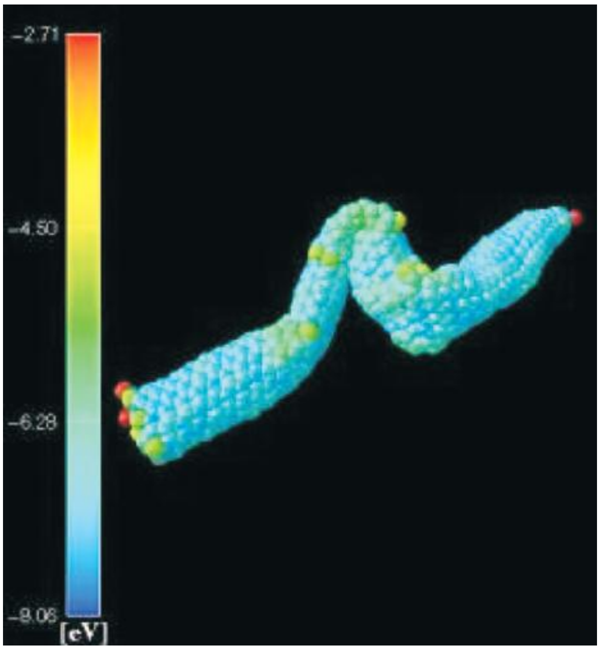
• phase transitions and self-assembly of atomic and molecular clusters [6-8];



• the influence of the molecular chirality on the structure of metal nanoparticles and the properties of nanopowders [9];

• fundamental basis of formation of fullerenes, nanotubes and their mechanical properties in the presence of effects [10-11];

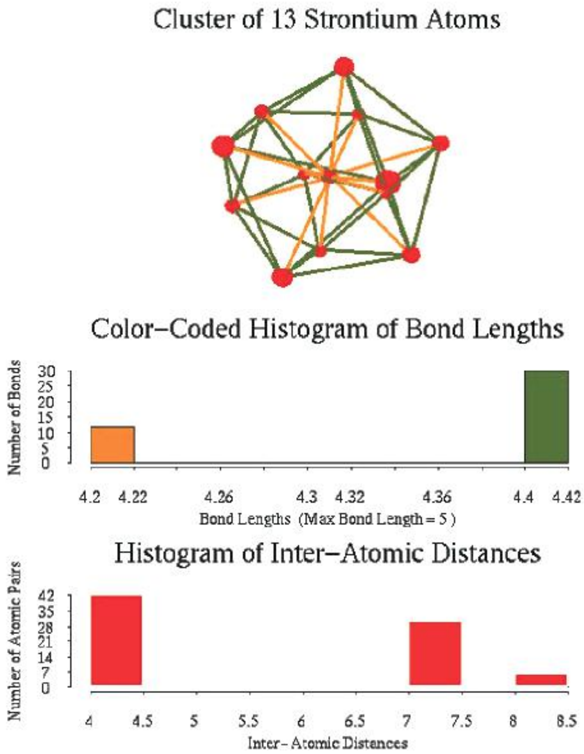
• adsorption and diffusion of gases on/in defective carbon nanotubes [12-13];



• special arrangements of metallic chromium clusters [14-15];

• predictions of the possible output of newly designed experimental equipments [16];

• transfer of knowledge: from nanoclusters to biosystems.



METHODS USED IN NANOSYSTEMS

When one deals with small systems, it is very important to distinguish between '<u>general properties of the substance</u>', say chromium, and '<u>size-specific properties</u>', say icosahedral clusters [6, 13]. Another issue is the time-dependence of a property as most nanosystems are metastable [17]. If thermodynamic, structural and dynamic properties are of interest [18], then the method of **molecular dynamics** provides this information.

A molecular dynamics simulation consists of stepping the system through its microstates. Ideally, one would like to keep the step size as small as possible since in the limit of zero step size the difference equations reduce to the exact differential equations. The error introduced by keeping a finite step size is the inherent truncation error of the method. The procedure, in brief, is as follows: from the molecular positions, the forces acting on each molecule are calculated; these are used to advance the positions and velocities through a small time step, and then the procedure is repeated. Principal features: Solution of Newton's equations of motion by a step-by-step algorithm; Simulation times from picoseconds to nanoseconds.

I and my students **have developed** modern software implementing the molecular dynamics method with various interaction potentials included into the Newton's equations of motion. My group's **achievements** in the field of phase transitions of small systems and their applications are world-wide recognized and highly cited. We have **invented a projection method** applied in the analysis of the phase space [19] and **related the self-organization of clusters to the protein-folding** [20].

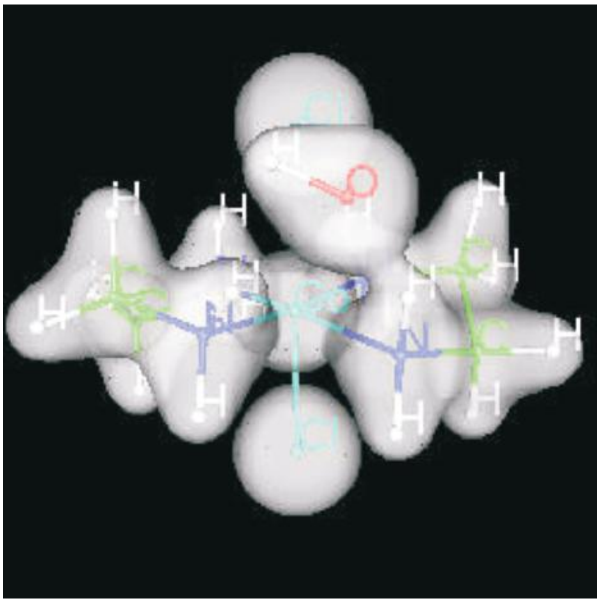
Invitations to write **topical reviews for** the high-level journals in **the US – Adventures in Chemical Sciences** [21] and **in Europe – the Journal of Physics** [22], and to give a talk at the conference in Istanbul organized by the Balkan Physical Society [23] were in recognition of these achievements.

Monte Carlo methods are often used when the configuration part of the complete phase space is better known. The Monte Carlo simulations give complementary information about the studied system by generating a Markov sequence of configurations. These are used to obtain the statistical (ensemble) average of the measured quantity.

There is no single Monte Carlo method; instead the term describes a large class of approaches. The best known is the Metropolis algorithm [24]. In a Monte Carlo algorithm at each stage, a random move of a molecule is attempted; random numbers are used to decide whether or not to accept the move, and the decision depends on how favorable the energy change would be. Then the procedure is repeated. Principal features: sampling configurations from a statistical ensemble by a random walk algorithm; no true analogue of time; possible to devise special sampling methods; provides thermodynamic and structural properties.

Utilizing the Monte Carlo methods we **have found** that in nanoclusters of chromium atoms **non-collinear atomic spins** can be observed [14-15] for selected sizes Fig., a phenomenon that is not possible in bulk of any substance.

The density functional theory (DFT) is a powerful quantum mechanical scheme, which treats the exchange and correlation effects in the substances in an efficient but approximate way. A reasonable accuracy for the structures of complex molecules and small clusters (up to several hundred of atoms) can be achieved by incorporating the DFT calculations [25] with some optimizing techniques - conjugate gradient method, steepest descent method, genetic algorithm [26], molecular dynamics. Despite the approximations used, many properties of the materials can be predicted on the basis of molecular structures: density of states, partial charges, and optical spectra. DFT calculations may help to move from a trial and error scheme to a systematic search for the optimal composition once the correlation between the optical non-linearity and the structural distortions is understood. Here we consider an example of dipole moment generation in octahedral metal complexes used as precursors of metal nanoparticles.



In order to understand why chains and spheres are formed by nanoparticles produced in boron-hydrate reduction process, we have considered several hypothetical replacements of atoms in the coordination complex [Co(en)2Cl2]+. Distortion of the trans-isomer, shown in the figure is observed when B replaces Cl inducing various shapes of nanoparticles via charge re-distribution in the complex after the modification.

FROM NANOCLUSTER STUDY TO BIO-MEDICAL CASES

Using a variant of the well-established BSP model we have shown that a properly working immune system may go wrong completely and attack "everything" [27]. This result has been obtained with the help of cellular automation with special rules implemented to mimic the reaction of the immune system to the drugs used in excess.

INTERNATIONAL ACTIVITIES OF THE MONTE CARLO GROUP

The group is a partner of the Nanoforum team [28] which provides information about the Nanotechnology achievements worldwide. Nanoforum was originally funded by the European Commission through FP5. Since July 2007 it has been operating as a European Economic Interest Grouping (EEIG), giving it legal status and the ability to enter into contracts with other parties, including tenders and new EU-funded projects. It will continue to provide news items from across the EU including information from projects and organizations, and can now offer customers a powerful advertising and dissemination service through its network of over 15,000 registered users and a website that attracts over 100,000 visits, 400,000 page impressions and 900,000 hits each month. Members of nanoforum.org: Institute of Nanotechnology, UK (Mark Morrison), CEA-Leti, Fr (Jean-Charles Guibert), VDI Technologiezentrum, DE (Holger Hoffschulz), Malsch Technovaluation, NL (Ineke Malsch), FFG - Austrian Research Promotion Agency, AT (Gerald Kern), Middle East Technical University, Department of Physics, TR (Rasit Turan), Unipress (High Pressure Research Center), PL (Witold Lojkowski), Sofia University, Faculty of Physics, BG (Ana Proykova), NanoNed (Leon Gielgens).

Within the framework of the project, we co-authored several important reports. The most recent have been *Nanotechnology in Aerospace* and *Nanometrology*. These reports can be freely downloaded from http://www.nanoforum.org/ [under Nanoforum reports].

The Nanotechnology in Aerospace report presents a concise introduction and contribution to the expert debate on trends in nanomaterials and nanotechnologies for applications in the civil aeronautics and space sectors in Europe. We explicitly exclude any military R&D and applications, as this falls outside the mandate of Nanoforum. Our target audiences are twofold: non-experts of an academic level with a general interest in the potential of nanotechnology for aerospace applications, and experts involved in setting the strategic R&D agenda in this field.

The **Nanometrology** report aims to provide information for a wide audience: academic researchers active in nanotechnology; engineers in industry; PhD students; researchers with experience in various measurement techniques who would like to enter the field of nanoscience, nanotechnology, and nanometrology; university and college teachers who would like to widen their knowledge in modern techniques and methods of material analysis; fundamental researchers who are interested in improvement of 'classical' theories that cannot explain the new phenomena emerging in the field of nanoscience; investors who would like to benefit from a future technology; SMEs with innovative programmes in their business plans. A wealth of figures, images and graphs give the reader the basis for understanding the peculiar field of nanosized objects and the materials made of them.

Funding Sources: The research conducted in this lab would not be possible without the support of the following organizations:

External Funding: FP5, FP6, NATO-CLG, JSPS-Japan, NSF (US), Bulgarian Science Fund

Internal Funding: The University of Sofia Fund for Research

References:

1. K. Binder in Applications of Monte Carlo Methods in Statistical Physics, Springer-Verlag, Berlin (1984).

2. Ole G. Mouritsen, Computer Studies of Phase Transitions and Critical Phenomena, Springer Series in Computational Physics, (Springer-Verlag, Berlin Heidelberg New York Tokyo 1984).

3. MP Allen, DJ. Tildesley, Computer Simulations of Liquids (Clarendon Press, Oxford, 1994).

4. W. Kohn and L. J. Sham, Phys. Rev. 140, 4A, 1133 (1965).

5. A. Proykova, in Nanoscale Magnetic Oxides & Bio-World, p.215-224 (Heron Press Sofia 2004) (ISBN: 954-580-156-5).

6. A. Proykova, D. Nikolova, and R.S. Berry, Symmetry in Order-Disorder Changes of Molecular Clusters, Phys. Rev. B 65, 085411 (2002).

7. A. Proykova, The Role of Metastable States in the Temperature Driven Phase Changes of Molecular Nanoclusters, Vacuum, v.68/1 pp.97-104 (2002).

8. Ana Proykova, Self- and Induced Organization of Nanoparticles (keynote lecture at The 1st NanoForum Workshop: Nanomaterials and Applications, Sinaia, Romania, October 5-7th, 2003 http://www.nanoforum.org/events/workshop/Proykova.pdf

9. A. Proykova, S. Pisov, I. Dragieva, J. Chelikowski,

DFT Calculations of Optimized Structures of Some Coordination Compounds, p.17 , Nanoscience&Nanotechnolgy'03, eds. E. Balabanova and I. Dragieva, (Heron Press Science Series, Sofia 2003) (ISBN 954-580-139-5).

10. A. Proykova and H.Iliev, Simulated Stress and Stretch of SWCNT, SIMS2004 eds. Brian Elmegaard, Jon Sporring, Kenny Erleben, Kim Sorensen, pp.273-279, (Copenhagen, 2004) (ISBN 87-7475-316 9) http://www.scansims.org/sims2004/tableOfContents2004.pdf

11. Hristo Iliev and Ana Proykova, Mechanically Induced Defects in Single-Wall Carbon Nanotubes, "Meetings in Physics @ University of Sofia", vol.5, pp.87-91 (2004) (ISBN 954 580-166-2).

12. Ana Proykova, Molecular Dynamics simulation of gas adsorption and absorption in Nanotubes, in Carbon Nanotubes Proceedings of the NATO Advanced Study Institute on Carbon Nanotubes: from Basic Research to Nanotechnology, Springer, Series: NATO Science Series II: Mathematics, Physics and Chemistry, pp.187-207, Vol. 222, eds. Popov, Valentin N.; Lambin, Philippe (Eds.) 2006, (ISBN: 1-4020-4572-7)

13. Evgeniya Daykova, Stoyan Pisov, and Ana Proykova, First-principle and Molecular Dynamics Simulations of Methane Adsorption on Graphene, p.209, Vol. 222, 2006, (ISBN: 1-4020-4572-7)

14. Ana Proykova and Dietrich Stauffer, Classical simulations of magnetic structures for chromium clusters: size effects, Central European Journal of Physics, v.3, No.2, pp.209-220 (2005)

15. Kalin Arsov and Ana Proykova, Antiferromagnetic versus Non-Collinear Arrangement of Chromium Clusters of Various Sizes, Nanoscience & Nanotechnology '05

16. H.S. Iliev, F.Y. Li, H.F. Lu, A. Proykova, Modulation of band-structure of defective single-wall carbon nanotubes under a transverse electric field,CP899, American Institute of Physics, p.718 (2007) (978-0-7354-0404-5/07)

17. A. Proykova, The Role of Metastable States in the Temperature Driven Phase Changes of Molecular Nanoclusters, Vacuum, v.68/1 pp.97-104 (2002).

18. A. Proykova, S. Pisov and R.S. Berry, Dynamical Coexistence of Phases in Molecular Clusters, J. Chem. Phys. v. 115, 8 Nov. p.8583-8591 (2001).

19. R.A.Radev, A.Proykova, F.Y.Li and R.S.Berry, Orientational Order-Disorder Phase Transitions in Plastic Molecular Clusters: Projection of Three-Dimensional Distributions onto a Two-Dimensional Surface, J. Chem. Phys. v.109, No.9, Sep.1, p. 3596 (1998)

20. K. Ball, R.S. Berry, R. Kunz, F.-Y Li, A. Proykova, D. Wales, From Topographies to Dynamics on Multidimensional Potential Energy Surfaces of Atomic Clusters, Science, 271(1996) 963.

21. A. Proykova, I.P. Daykov, R.Stephen Berry, Second- and First-Order Phase Transitions in Molecular Nanoclusters, Adventures in Chemical Physics 132, 131-150, (2005).

22. Ana Proykova and RS Berry (invited topical review) Insights into Phase Transitions from Phase Changes of Clusters, J. Phys. B: At. Mol. Opt. Phys. 39 (2006) R167-R202.

23. A. Proykova, Topology of the potential energy surface and the origin of phase changes in finite atomic clusters, CP899, American Institute of Physics, p.69-73 (2007)

24. Metropolis, N. and Rosenbluth, A. W. and Rosenbluth, N. M. and Teller, A. H. and Teller, E., J. Chem. Phys., 21, 1087, (1953).

25. A. Proykova, S. Pisov, I. Dragieva, J. Chelikowski, DFT Calculations of Optimized Structures of Some Coordination Compounds, p.17 -22, Nanoscience&Nanotechnolgy'03, eds. E. Balabanova and I. Dragieva, (Heron Press Science Series, Sofia 2003).

26. S. Pisov and A. Proykova, Optimization of Molecular Clusters Configurations using a Genetic Algorithm, in "Meetings in Physics @ University of Sofia" ed. A. Proykova, v. 3, p.40 (Heron Press Science Series, 2002).

27. Dietrich Stauffer and Ana Proykova, Cellular Automata Simulation of Medication- Induced Autoimmune Diseases, Physica A: Statistical Mechanics and Its Applications, v.331, p.545-551(2004).

28. http://www.nanoforum.org/

BULGARIAN ADDED VALUE TO ERA

NANOSCALE STATE – UNITY OF ALIVE AND NON-ALIVE MATTER

Iovka Dragieva, President of the National Coordination Council on Nanotechnologies at the Bulgarian Academy of Sciences
Acad. G. Bontchev St., Block 10, 1113 Sofia, Bulgaria

WHY NANO?

Development of science and research nowadays aims at improvement of the quality of life of people and their physiological reproduction and survival, intellectual and spiritual development, keeping the harmony and balance in the nature of alive and non-alive matter on our planet.

Rapid development of possibilities for precise investigations at large magnification and observation of the real atomic order of samples through discovery of the scanning tunneling (1981) and atomic force microscopy (1986) followed after the second half of the last century. Opportunities were created for visualization and suitable registration of any kind of information in the media for digital, optical and sound memory with high density recording and reproducing, including for perception by all sensitive organs of the human body.

Since the years of Poling and Feynman [1] and discovering of DNA double helix, by the possibilities of research investigations and knowledge evolution, the attack on studying the nanoscale state has begun. Formally in June 1993 during the two-week NATO Advanced Study Institute course on the Corfu island, Greece, Richard Siegel proposed to use "nano" (for size 10^{-9} m), instead of the word "angstrom" (size 10^{-10} m), which at pronouncing in English acquired dialectal sounding depending on the nationality of European or American researchers [2]. During the subsequent years new and appropriate technological tools for multiple and reproducible production of nanoscale materials (or nanotechnology) were hold out for the study of nanoscale state. At the beginning "up-down" and "down-up" approaches were proposed. In the first variant it was proposed to attain nanoscale state via milling, breaking to pieces of big, with micron size, volumes till nanoscale phases are attained. But very soon it was established that at creation of nanosized objects by nanotechnological means, building atom after atom (0D, 1D) in two-dimensional (2D) or three-dimensional (3D) organized structures as clusters, particles, quantum dots, nanotubes, nanowires, nanopipes, etc., it is possible to realize shortening of the internuclear distance between the two closest neighboring atoms. The established and proved remarkable property of decreasing the internuclear distance at forming of the diatomic molecule and resulting quantum-sized effects at nanoscale state transferred the *"nano"* problem to all objects of the alive and non-alive nature. In this way the nanoscale state as a *state of shrinking matter* [3] enriches our knowledge of the origin and organization of the universe and space, of the human being, of variety of animals and plants.

For all nanomaterials with observed so-called quantum-sized effects, the decrease of internuclear distance between two closest neighboring atoms is proved. As a result overlapping of orbits of the most inner, closest to the nucleus two 1s electrons occurs, and the binding energy of electrons to the nucleus begins to differ with considerable value of several eV, and their vibrational oscillation frequencies become definitively measurable and estimated to about 500 femtoseconds (1 femtosec = 10^{-15} sec) and 800 femtoseconds respectively. Experimental demonstration of this fact was a sufficient ground for the Nobel Prize in chemistry in 1999 for Ahmed H. Zewail. In this way the traditionally studied different types of chemical bonds lost their common definition or "name" acquired and used for many years. More important in this case is that one and the same chemical elements, already studied and well-known to us, take part in organization of all substances from the alive and non-alive nature. Only the bonds created between them are with different energy, relative length and spatial position in the n – dimensional space.

Another particularly stable system can be discussed – the human body, which as a composition contains four lightest elements – hydrogen, nitrogen, carbon and oxygen up to 96.6 wt. % [4]. Quantum-sized effects, i.e. the fluctuations in oscillation frequency of the electrons round the nucleus are most probably expected at organization of bonds between atoms of these elements. The other two comparatively "heavy" elements – calcium and phosphorus – supplement the weight composition of the human body up to 99.1 wt. %, and only 0.9 wt. % remain for all the rest 24 elements participating in the chemical content of our body and its functional systems, producing energy of different types and quantities. "Hydrogen" bonds (of hydrogen with nitrogen and hydrogen with oxygen) connecting the four bases of DNA are another interesting example. After discovery of DNA double helix fifty years ago there followed a clarification of the rules for connecting these four bases. With the help of nanotechnological tools now it is possible quickly to identify the origin of the cell material and its recognition – if the found DNA object [4] is from a human body, from animals, insects or is of bacterial origin.

Quantum-sized effects of the nanoscale state predetermine phenomenal properties and possibilities of this type of materials in relation to conductivity, magnetic and dielectric permeability, optical properties, microhardness and elasticity, corrosion and wear resistance. The knowledge of nanoscale state has already found direct realization in such industries as electric and nuclear power engineering, transport, life science, environmental science, biotechnologies and gene engineering, aerospace equipment, defense, pharmacology and medicine, in packing, for storage and making foodstuffs tastier, in textiles and synthetic flooring manufacture, in footwear industry, construction, lighting facilities, etc.

Specific differences exist between educational programs at schools and universities in various countries on different continents in such basic subjects as physics, chemistry, biology, geology and earth sciences, mathematics. This is a problem in building of the future researchers and creators in this field of multidisciplinary knowledge. In December 2003 a Euronanoforum was organized in Trieste, Italy with over one thousand participants from 5 continents. There this difference was demonstrated very clearly both for knowledge of the quantum level and in researchers' visions and expectations with regard to engineering and medical applications of nanomaterials in a global economy. For the first time it was debated that application of nanomaterials in the common practice puts forward a number of ethical problems. From the moment of creation of human embryo till the moment of desired or ordered lethal outcome with the help of nanotechnologies decisive moments of human life are commercialized or criminalized. It is also an ethical problem how state institutions are admitted and will be allowed in the future to get access to personal data, including hereditary diseases and genetic defectiveness, state of health, financial security, freedom to be mobile, to communicate, etc.

Implementation of nanotechnologic achievements in information systems and communications leads to loss of personal freedom, the initiative and the individuality of people [5].

A short time after that attempts were made in the Far East (Singapore, China – Hong Kong) in creation of symbols representing the meaning of the "nano"-effects. In the same context the currently offered logo (represented as a figure at the title of the present article) from the NANOTEC2008 conference held in March 2008 in Italy is very successful and good, because it expressively and clearly, on a quantum level, answers the question – what is NANO and why *NANO*scale state and knowledge improvement form an exceptional priority for the world.

DEVELOPMENT OF RESEARCH INVESTIGATIONS ON NANOSCALE STATE IN THE WORLD

The USA are among the first countries that judged possibilities of the nanoscale state on their merits and started active research activity with investments similar in quantitative parameters to those of Japan.

In 1996 an exceptional book by E. Budevski, G. Staikov, and W.J. Lorenz was published [6], which combines the macroscopic and modern atomistic approach to theories of nucleation and growth, well illustrated by experimental examples, with the new surface imaging techniques such as STM and AFM.

Already in 1997 there were signed bilateral projects on the subject between the National Science Foundation (US) and the Bulgarian Academy of Sciences with partners K.J. Klabunde and I. Dragieva respectively.

In 1998 Prof. Lorenz in person was on a visit to BAS and Prof. Budevski, in order to initiate establishment of a research community in our country in the field of nanoscience and nanotechnologies. In the text of the well-known president Clinton's National Nanotechnology Initiative (NNI) [7] of 2000 on the known theoretical mechanisms of nucleation the names of Bulgarians Stranski – Krastanov are mentioned. During the same year a monograph on a fundamental problem of nucleation by a representative of the outstanding Bulgarian physicochemical school was published by the prestigious Oxford Publishing House [8]. Budgetary means for NNI and PCAST (2005 – the National Nanotechnology Initiative at Five Years) increase 9 times since 1997 to 2005 and their share is 26.4% of the total world investments, while the share of the EU is 25.6% and the share of Japan – 23.2%.

On June 1, 2007 the Council of Ministers of the Russian Federation took a decision on establishment of a Governmental Council on Nanotechnologies, which is created within the framework of the President's initiative *Strategy for Development of Nanoindustry.* The Governmental Council on Nanotechnologies is guided by one of the vice Prime Ministers of the Russian Federation. The New Council works permanently, providing interaction between federal administration, business society and research sphere. 28 billion rubles will be spared for development of an appropriate infrastructure. It is supposed that nanotechnologies will be in the basis of the new systems of defense and will be used in many other branches of industry, medicine, transport, aerospace, and telecommunications. During the recent years Russia has invested in nanotechnologies about 150 billion rubles through different federal programs. Part of the money of "UKOS" Petrol Corporation paid in the budget of the country (about 400 billion rubles) is given for establishment of a Corporation on Nanotechnologies.

Since June 2005 the European Commission has adopted a European Action Plan *Nanoscience and Nanotechnologies 2005-2009*. It provides for:

• servicing and training of the society – the young in particular;

• development of new models and means of communication, dialogue and engagement;

• increase of the role of individual choice via development of scientific culture of the society;

• provision of access to checked information on ethical, social and legal aspects of nanotechnologies.

This plan was accepted by all member states of the EU and four strategic directions for research and implementation were included into the 7-th Framework Programme (2007-2013): Nanosciences and nanotechnologies, Materials, New production technologies and Integration of technologies for industrial applications.

EC will invest 3.5 billion euro in projects in these directions, and for the years 2007 and 2008 are envisaged about 300 – 400 million euro each. The interest of European countries in the topic *Nanoscience and nanotechnologies* is huge as this is the sphere which requires high degree of research efforts consolidation and integration of supplementing skills of scientists, teachers, researchers and producers. In essence this is the economy of the XXI century – the knowledge-based economy.

NATIONAL COORDINATION COUNCIL ON NANOTECHNOLOGIES AT THE BAS – STRUCTURE AND DEVELOPMENT OF INVESTIGATIONS ON NANOSCALE STATE IN BULGARIA

National Coordination Council on Nanotechnologies established by the decision of the Managing Board of the Bulgarian Academy of Sciences, record of proceedings No. 2 of 03.02.1999 (and appointed by the Order No. I-187/ 22.03.1999) in the year 2000 constituted National Center on Nanotechnologies (NCNT) at BAS headed by academician Evgeni Budevski (at present he is our Honorary President) [9]. In the course of 9 years this virtual structure of a network type performs successful coordinating activity in educational process and research investigations and takes care of the development of research potential in the field of nanoscale phases and nanotechnology science in the country. We are proud that its activity led to increase of the competence in this sphere in Bulgaria [9] www.bas.bg/nano.

The following topics mentioned below are chosen as main structural directions typical for research carried out in the country:

Theory Modeling and Simulations;

Clusters, Nanoparticles, Composites;

Thin Films, Superlayers, Quantum Dots and Nanowires;

Nanophases in Bulk Materials. Nanocomposites;

Bio-inspired Concepts and Medical Aplications;

Micro and nano engineering. Nanometrology.

Organization of the annual Workshop "Nanoscience & Nanotechnology", for the first time held on May 14-15, 1999, is a good tradition and main activity of NCNT. The above-mentioned subject directions are working poster sessions. Invited lecturers from more than twenty countries from Europe, Asia and America took part in these conferences with international participation. After reviewing the presented original papers are published in the scientific series "Nanoscience & Nanotechnology (Nanostructured Materials Application and Innovation Transfer)" as volumes from № 1 to № 7 (2007) with editors: E. Balabanova and I. Dragieva. Printing of materials from the Ninth Workshop held in November 2007 as volume № 8 is expected.

While in the year 2000 only 65 contracts were worked out, the number of implemented projects has tripled in the following years. The activity of the National Center on Nanotechnologies at BAS is highly appreciated and supported within the bounds of possibility of the Central Administration of BAS and institutions that participate in it – 21 institutes and central laboratories, ten universities (some of them separately with two or more faculties), with marked interest in 2007 on the part of universities in the country to join in the work of the Council.

The ninth year of NCNT at BAS is characterized by some peculiarities:

• Liveliness is observed in conducting of research seminars on the subjects;

• The number of research contracts remains approximately the same compared to the recent years, and the number of PhD students on the subjects remains the same;

• Publishing activity has increased (about 4 times) in comparison with the year 2000 and reached about 400 publications by Bulgarian researchers from 18 institutions of the Center in international scientific press.

The above-mentioned facts from the activity of NCNT impose some generalizations.

High publication activity is a lasting trend, as well as registered permanent active participation of about 150 to 300 persons in our annual conferences.

As satellite initiatives in the work of the annual Workshop were:

(i) in 2003, 2004 – COSENT initiative (**CO**operation of **S**outh-east **E**uropean countries in the field of **N**ano**T**echnology – UNESCO, Contracts # UVO-ROSTE 875.589.2,875669.3, 875.617.4;

(ii) in 2004 - FP6 Project NENAMAT(**Ne**twork for **Na**nostructured **Mat**erials of Associate Candidate Countries – SSA-INCO-CT-2003-510363;

(iii) in 2005 - FP6 Project – NoE-4M(Multi Material Macro Manufacture).

As special initiative in 2005 Satellite Meeting "**Bulgarian Women in NANO 2005**" was held at combining the foreseen investigations on participation of Bulgarian women as researchers in this field of knowledge from three financed projects:

FP6 Project NENAMAT–INCO–CT–2003–510363;

FP6 Project WomenInNano–SSA–2005–016754;

FP6 Project NANOPHEN–INCO–CT–2005–016696.

Obviously exhaustion of research opportunities at the available contingent of people and equipment on the subject in our country is on the way. But the awaited trend is the well-outlined *policy of the EU to improve knowledge on the nanoscale state through cooperation of researchers in international teams*, for which the activities of our center have contributed to a considerable extent.

National engagement with the problem of knowledge improvement on nanoscale state has not been sufficiently manifested yet. Limited financial resources allocated from the GDP for training and research do not afford possibilities to our structure to develop its real potential and to meet modern requirements to development of this sphere of science and technology in Bulgaria, although our country is among the first countries that actively joined in this process.

The problem of better financial support for publication of information materials on the subject, contacts with media and popularization of opportunities offered by implementation of nanotechnologies in all spheres of economy, which without any doubt will lead to better practical realization of these scientific investigations in the country, is left open.

Finding out of adequate organizational-structural solutions of the National Coordination Council on Nanotechnologies at BAS is also one of the main problems. It is required from our country as a new member state of the EU (since January 1, 2007) and in accordance with the EU's document "The Community Framework for State Aid for R&D and Innovation" valid till the year 2013 and published in [10].

As non-aggressive but competent and fascinating knowledge and science for nanoscale state develop and assume a unity between alive and non-alive matter on the basis of atom organization of chemical elements in billions combinations, it should be expected that training, education and research will find the best way for restructuring their activities for improvement of the quality of life and for saving the life on our planet.

References:

1. R.P. Feynman, Eng. Sci. 23, 22(1960).

2. Nanophase Materials, edited by G.C. Hadjipanayis and R.W. Siegel, Kluwer Press, Dordrecht, 1994, Proc. of NATO- Advanced Study Institute, June 1993, Corfu, Greece.

3. National Geographic Magazine Bulgaria, 2006, 6 (8) 2006 г, pp. 40 – 61.

4. Handbook of Chemistry and Physics, A Ready-Reference Book of Chemical and Physical Data, 85th Edition, 2004-2005, Ed. David R. Lide, CRC Press, Boca Raton.

5. The Ethics and Politics of Nanotechnology, UNESCO- Division of Ethics of Science and Technology, Social and Human Sciences Sector (June 2006), http://www.unesco.org/shs/ethics

6. E. Budevski, G. Staikov, W.J. Lorenz, Electrochemical Phase Formation and Growth (An introduction to the Initial Stages of Metal Deposition), VCH, Weinheim, 410 pp.

7. http://www.nsf.gov/crssprgm/nano

8. D. Kashchiev, Nucleation: Basic Theory with Applications, Butterworth-Heinemann, Oxford, 2000, 544 pp.

9. www.bas.bg/nano

10. Official Journal of the European Union, 30.12.2006, C323/1-C323/26.

THE NATIONAL PROGRAM ON NANOSCIENCE AND NANOTECHNOLOGIES (2005–2007), A PART OF THE EU FP6–THEME 3 & FP7–THEME 4 "NANOSCIENCES, NANOTECHNOLOGIES, MATERIALS AND NEW PRODUCTION TECHNOLOGIES – NMP"

Ana Proykova, Vice-president of the National Council on Nanotechnology, Program Committee Member of the EU FP7-Theme 4

INTRODUCTION

There has been considerable interest in investigating the properties of systems at the nanoscale since Feynman uttered the famous phrase "There is plenty of room at the bottom" (1957). Nanotechnology describes the creation and utilization of functional materials, devices and systems with novel functions and properties that are based either on geometrical size or on material-specific peculiarities of nanostructures. Purely geometrically the prefix "nano" (Greek: dwarf) describes a scale 1000 times smaller than that of present elements of the micrometer-sphere (1 nm corresponds to the millionth part of a mm). In the nineties of the 20th century, the prefix 'nano' in the title ensured easier funding of research proposals which, in general, focused on the fundamental research or, at most, lab prototypes of possible applications. With the discovery of techniques to organize, characterize, and manipulate individual elements of matter as well as the increasing insights into self-organization principles of these elements,the world-wide industrial conquest of nanoscale dimensions began. In the meantime the speed of innovation led to the situation that physical fundamentals are still being investigated, while first product groups are already entering the world markets. Their sales impacts are caused by the implementation of nanoscale architecture with new macroscopic functions.

In this milieu the Bulgarian researchers have been recognized by the international scientific community due to their theoretical results, published in international journals. Most of the Bulgarian researchers have been partners in international collaborations that helped them to stay in the front line during the difficult years of extremely low funding in the country. Needless to say, with a small number of exceptions, the recognized results were shared by all partners with a predominant ownership of the funding country. Hence the output products could not be used by Bulgarian companies without acquiring a license. Practically the achievements of our researchers have not been used by our companies.

OBJECTIVES

The principle objectives of the NMP program are to improve the competitiveness of Bulgarian industry as a part of the European industry and to generate knowledge to ensure its transformation from a resource-intensive to a knowledge-intensive base, by creating step changes through research and implementing decisive knowledge for new applications at the crossroads between different technologies and disciplines. This will aid both new, high-tech industries and higher-value, knowledge-based traditional industries, with a special focus on the appropriate dissemination of RTD results to SMEs. These activities are important for qualifying technologies, which impact all industrial sectors.

The program aims to fund research and development projects that will effectively contribute, either on their own or by enabling further development, to the aimed transformation. This transformation is essential in order to produce, in a sustainable manner, high added value products, embedding cultural values of both national and European dimensions

STRATEGY OF THE NATIONAL PROGRAM IN NANOTECHNOLOGY

• To link the research groups at the universities and Bulgarian academy of sciences with the high-technological companies ready to invest in hew production lines

• To develop interdisciplinary curricula at the universities that cover the necessary knowledge for the modern field of nanotechnology

• To educate and train young researchers and workers at high-tech companies in the field of nanotechnology in a way to meet the requirements of the 21^{st} century

PRIORITIES

1. Material science of nano-sized materials, including nano-powdered ceramics, composite materials containing nanocrystals or powders, materials based on carbon-tubes or fullerenes, nanoparticulate coatings, nanostructured metals and alloys;

2. Thin layers and multi-layered nanosystems for applications in **information processing, storage and transmission** (nanoelectronics, materials and devices, optoelectronics / optical materials and devices, magnetic materials and devices, organic (opto) electronics, nanomechanical materials and devices;

3. Molecular and atomic design for drug encapsulation, targeted drug delivery, molecular recognition, biocompatible materials and layers, molecular analysis, DNA analysis, biological / inorganic interfaces and hybrids, diagnostics, molecular recognition;

4. Long-term research with generic applications: self-assembly, quantum physics / mesoscopic systems, chemicals interfacing to organic / biological molecules, ultra-precision engineering;

5. Nanometrology and applications – analytical equipment and techniques, powder production and processing, deposition equipment and techniques, patterning equipment and techniques, ultra-precision metrology.

AIMS AND APPROACHES

Bulgaria's position still needs to be strengthened in the research activities related to nanosciences, nanotechnologies, materials and production technologies within the highly competitive global context. The competitiveness of industry will largely depend on new knowledge and on new ways of integrating and exploiting the existing and new knowledge. Bulgaria can benefit from its respected scientific position in specific fields through bringing specialist disciplines together.

A key issue is to integrate competitiveness, innovation and sustainability into the research activities covered by NMP as well as initiatives capable of fostering the dialogue with society at large. Research has to be complemented by activities aimed **at education** and **skills development** addressing the more long-term research issues underlying many technology fields. Nanotechnology Masters Courses to be developed and offered to the students at Sofia University, Technical Universities in Sofia, Varna, Rousse, Chemical Technology and Metallurgical University, each varying in their emphasis and content.

RESULTS (2007)

The increased funding of nanosciences and nanotechnologies by the National Science Fund in the period 2005-2007 has a significant output: numbers of patents; involvement of SMEs in consortia funded by international funding agencies (the European Framework Programmes, NATO for science, UNIDO - Japan).

Five projects operated by teams from (at least) three different institutions have been funded in 2006 for a three-year period of research each. The amount of money exceeded 10 times the size of the usual (for the country) amount of funding, letting the researchers modernize their equipment.

The newly established master programs based on learning-by-working approaches at Sofia University (Faculty of Physics: master programs on '*Nano-optoelectronics and Information Technology*' (a joint program with the Faculty of Mathematics and Informatics) and on '*Nanotechnologies for quantum systems applied in optoelectronics*'; Faculty of Chemistry: '*Nanomaterials and Nanotechnologies*') have been partially funded by the National Science Fund via the Call 'Unique Infrastructures'.

VISION FOR THE NEAR FUTURE

Bulgaria has established a strong knowledge basis for the rapid development of nanoscience and nanotechnologies. Nevertheless, the field needs more fundamental knowledge and skills in transferring the lab prototypes into the real economy. Recently, many products have been enhanced by nanotechnology and are on the market – coatings, textiles, paints, sport equipment.

As part of the strategy for development of the NMP, the reinforcement of scientific excellence must be accompanied by the development of world-class infrastructure to ensure that a critical mass is assembled at national and European level. Investment in human resources is needed to bring forward the new generation of researchers, engineers, and related specialists. Having in mind that the main feature of nanoscience and nanotechnologies is bridging specialists from a wide range of disciplines to understand and exploit phenomena at the nanoscale of matter, we should focus in building of nanotech research infrastructures. Nanotechnology provides unique opportunities for creating knowledge-based enterprises and bringing our economy further up.

The scientific and technical challenges are ahead of the researchers in the field of nanoscience and nanotechnology. These require excellence in research and development (R&D) in order to ensure that our country would be competitive in a long term. In this respect, **the support of the R&D through public funding is essential together with the availability of world–class researchers.**

Public investment in nanotechnology R&D has been significantly lower than our main competitors' in Europe and the region the last decade. Despite the improvement in 2006/2007 in funding, it is still behind the limits which are needed for the field, defined in the Lisbon objectives – we need a factor of ten by 2010. Appropriate **synergy of national funds with the structural funds** will help the fiscal status of the field. Another approach – very important for our country – is **merging the field of nanoscience with the Life Sciences** (including biotechnology, medicine, and pharmacy) and **with the Environmental Sciences** (including cleaning of water resources).

The transfer of scientific achievements into everyday life applications can be stimulated via **a national program**, coordinated in a way to meet the requirements of the European Union. Initiatives of the European Union such as Open Method of Coordination and ERA-NET-Plus can support the process.

MADE IN BULGARIA WITH EUROPEAN SUPPORT

ATOMIC VAPOR NANO-LAYERS – A NEW TOOL OF THE LASER ULTRA-HIGH RESOLUTION SPECTROSCOPY

Stefka Kartaleva, Dimitar Slavov
Institute of Electronics, Bulgarian Academy of Sciences
72, Tsarigradsko shousse Blvd., 1784 Sofia, Bulgaria

The Doppler effect is related to the propagation of harmonic oscillations (optical, acoustic) and consists in oscillation frequency change with the propagation of its source. The Doppler effect is of fundamental importance in laser spectroscopy. The atoms and molecules in the ensemble under observation perform continuous movements with velocities grouped around one central frequency value, which is determined by the ensemble's temperature. This temperature movement of atoms leads to a spectral broadening of the transitions and so limits the application of many devices and methodologies. For atoms enclosed in cells with centimeter-scale size, the laser beam "sees" the atomic ensemble in the same way – with the same velocity distribution of atoms independently of the propagation direction trough the cell. In this case we say that the velocity distribution of atoms is spatially isotropic.

New kind of cells was developed in the last couple of years for laser spectroscopy. They contain atomic vapors of different metals (mainly alkali metals). The dimensions of these cells differ significantly in different directions (Fig. 1). The distance between their high-quality windows L is on the order of 10 μm. However, the windows diameter is about 1–2 cm. Therefore, a strong spatial anisotropy is present for the time of interaction between the atoms and the laser radiation. For example, Cs atoms (Fig.1, $\nu_{\perp}$), which average thermal velocity at room temperature is on the order of 200 m/s, will fly the 10 μm distance for about 50 ns. Such a limit is not imposed on the atoms (Fig.1, $\nu_{\parallel}$), moving parallel to the windows of such kind of cell. They will interact with the laser radiation for a time determined by the diameter of the laser beam

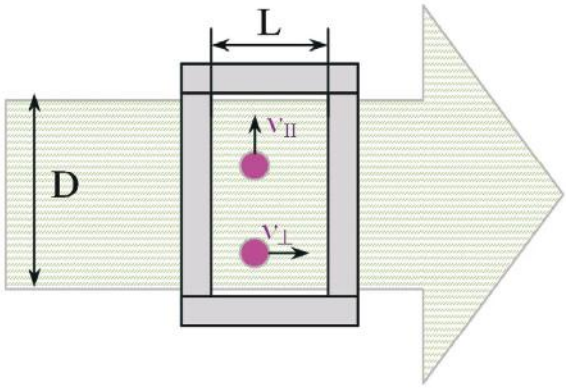


Fig. 1. Atoms in nanocells

D. When the cell is irradiated with a laser beam propagating orthogonally to the window surfaces, the atoms with velocity direction close to parallel to the window surface can be considered as "fixed", which leads to a strong reduction of the Doppler effect and to the related Doppler broadening of the spectral lines as well. From the point of view of the laser beam two kinds of atoms can be seen – "slow" (moving parallel to the windows and therefore having very small projection of the velocity vector on the laser beam propagation direction) and "fast" (moving parallel to the laser beam propagation direction in the narrow space between the cell windows).

The second-generation extremely thin cell (Fig. 2), developed by Armenian scientists, allows the formation of an atomic nanolayer (L=100–1500 nm). The initial experiments performed by scientists from the Armenian Academy of Sciences and from the Paris-Nord University justify the expectations for a new direction in the ultra-high resolution laser spectroscopy to be created, where the investigated medium has at least one dimension of the order of the laser wavelength λ.

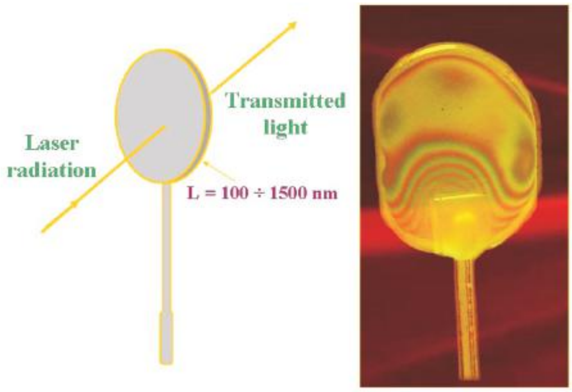


Fig. 2. Scheme and realization of a nano-cell

With the new nano-cell the presence of the two groups of atoms mentioned above leads to observation of a big difference between the fluorescence and transmission spectra (Fig. 3). Here the basic contribution to the creation of fluorescence signal belongs to the atoms moving parallel to the windows. The fast atoms moving along the laser beam direction do not have enough time to perform a complete absorption-emission cycle, i.e. to fluoresce. As it can be seen from Fig. 3, because different groups of atoms contribute to the fluorescence and absorption, a big difference in the width of the corresponding optical transitions in each case occurs. The transitions are completely resolved in the fluorescence case. Only the "fast" atoms are able to contribute to the absorption spectrum in the nano-layer because the absorption of a quantum of light is a process a lot faster. In this way the absorption process "suffers" much more from the Doppler effect. It is worth to mention here that in the cm-size cells different Cs-transitions are completely overlapped and cannot be separated. In this manner the nano-cell gives the opportunity for obtaining better resolution in laser spectroscopy as well as to study the dynamics of the absorption and fluorescence in more details.

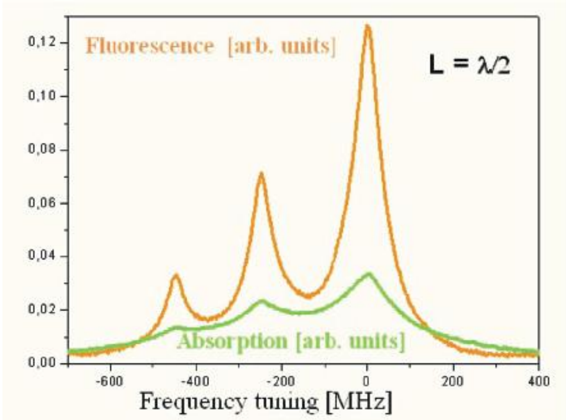


Fig. 3. Dramatic difference between the absorption and fluorescence of Cs atoms nano-layer

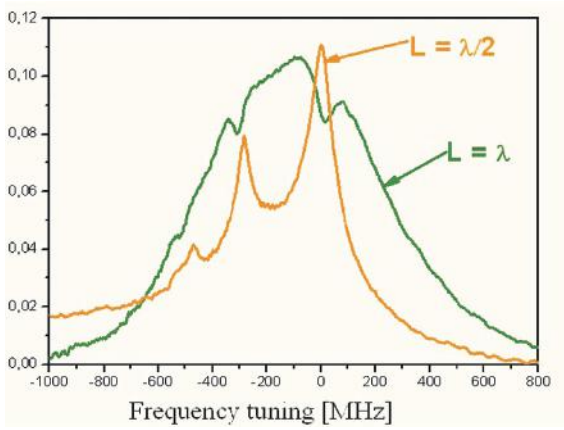


Fig. 4. Absorption spectrum of Cs nano-layer with thickness L = λ/2 and L = λ

The further investigations show that the atom confinement between two surfaces spaced one to the other at less than (or in the order of) the light wavelength results not only in elimination of the Doppler broadening. In such an ensemble a series of coherent effects occurs, which are subject of intensive study recently. Among them we shall note the Dicke effect observed in the optical part of the spectrum. The big difference between the absorption spectra shown in Fig. 4 for two Cs nano-layers, the first with thickness L=λ/2, and L=λ for the second, can be easily seen. The first interesting conclusion is that after increasing two times the thickness of the Cs-layer its maximal absorption does not increase about two times. Even on the contrary – in the center of the strongest transition the absorption at $L=\lambda/2$ is bigger than at $L=\lambda$. The reason for that is the coherent response of the medium as a result of the Dicke effect, which is the strongest at $L=\lambda/2$ and disappears at $L=\lambda$. The second interesting detail is in the big shape difference in the two spectra for two different thicknesses of the Cs-layer. Theoretical explanation leads to a new fundamental knowledge about the atom-light interaction.

The Institute of Electronics in the Bulgarian Academy of Sciences is coordinating a European contract in the INTAS program (grant: 06-1000017-9001) named: "Study of atomic vapor layers of nanometric thickness and atom-surface interaction". Partners on the project are two laboratories from France and one from Italy, Armenia and Latvia respectively. Under the project essential efforts are applied to study the new properties of the thin metal-vapor atomic layers. The Coherent Population Trapping resonances obtained are very sensitive to weak interaction between the atoms and the cell surfaces. They are promising for investigation of gas-surface interaction.

In the domain of laser spectroscopy of metallic-vapor nano-layer teams from the Institute of Electronics, Sofia University and Paris-Nord University collaborate under the scientific program "Rila".

These investigations and the knowledge obtained are very important for development of compact optical magnetometers with high spatial resolution of the measurements without compromising their high sensitivity. The narrow resonances registered allow the application for laser frequency stabilization, high-precision optical clocks and magnetometers. Further prospective is the investigation of the coherent effect in atoms confined in 2D and 3D micro- and nano-volumes using hollow optical fibers and porous media. This will strongly enforce their efficiency for development of optical sensors with micrometric dimensions.

The sensors based on the coherent interaction between atoms and light show parameters promising for different modern applications. One of the problems is related to their miniaturization to micrometric scale without compromising their properties. Moreover, recent active investigations for obtaining narrow coherent resonances in solid media (much more suitable for applications) are still not successful. That is why we consider the coherent resonances obtained in the intermediate case of atomic vapor confined in miniature volumes as a very prospective method for development of new sensors and new methodology in photonics.

EQUAL IN EUROPEAN RESEARCH AREA

BULGARIAN VIPs

Prof. IOVKA DRAGIEVA, DSc
National Centre on Nanotechnology (NCNT), Bulgarian Academy of Sciences
E-mail: iovka@cleps.bas.bg

Leader of the "Nanoscale Materials" department of the Institute of Electrochemistry and Energy Systems at the Bulgarian Academy of Sciences

Prof. Iovka Dragieva is one of the leading scientists in the field of nanoscale particles production by means of chemical processes in aqua solutions and metal particles applications with more than 170 scientific articles and 27 patents (USA, Japan, BRD, the Netherlands, Bulgaria incl. 2 patents for materials of dentistry). Original technological processes and reactors for production of metal clusters, metal nanoparticles, ferromagnetic nanoparticles, hybrid nanoparticles as nanowires, core/shell products incl. metal clusters on carbon nanotubes are objects of her interest. Their chemical composition could contain one, two or more elements selected from the list of 42 chemical elements. She is Bulgarian co-ordinator of two NSF-USA /BAS – Bulgaria joint projects – INT-9727193 and INT-0124080 on nanoscale particle production, Leader-Invest. Proposal Acronym PROMETHEAS,ICA2-CT-2002-1001 FP5RTD., National Contact Person of Bulgaria for Priority 3 and Member of the Program Committee for Priority 3 "Nanotechnology and nanoscience, knowledge-based multifunctional materials, new production processes and devices" of the 6th Framework Programme of European Communities, President of the National Coordination Council on Nanotechnology of Bulgaria (www.bas.bg/nano/), member of Amer. Chem. Soc. and IEEE Soc., participant in "Network for Nanostructured Materials of ACC", acronym NENAMAT, FP6-2003-ACC-SSA- GENERAL, PL 510363, and in Coordination Action " CO-ORdination by Best Practice Exchange and on Knowledge Building by NMP-NCP's in an Enlarged European Research Society" - COOREERS, FP6-2003-Ti-3-ncp, P - 011800.

Prof. Dragieva is the leader of the " Nanoscale Materials" department of the **Institute of Electrochemistry and Energy Systems** at the Bulgarian Academy of Sciences – www.bas.bg/cleps/ (former **Central Laboratory of Electro-chemical Power Sources**), which consists of 7 Departments devoted to R&TD of batteries and fuel cells. Evaluated as *Centre of Excellence* (since 2003, EC, EU), the Institute has more than 30 years of experience in fundamental electrochemical studies including electrochemical phase formation and growth, electrocrystallization, TEM/SEM imaging, XRD, X-ray microprobe analyzer of solid surface, nanoscale materials, catalysts and electrocatalysis preparation and investigations. **IEES** offers original technological processes and reactors for production of metal clusters, metal anoparticles and metal nanowires. The original methods provide flexibility for control of the nanoparticles structure and size (3 to 100 nm) and their self-organization as chains and nanowires according to the desired applications. IEES is a member (and host institute) of the National Centre of NanoTechnology of Bulgaria (NCNT-www.bas.bg/nano/ and www.cosent.dir.bg).

Assoc. Prof. VALENTIN POPOV, DSc
Faculty of Physics, University of Sofia
5, J. Boucher Blvd., 1164 Sofia, Bulgaria
E-mail: vpopov@phys.uni-sofia.bg

Over 100 publications - papers and reviews, in journals with impact-factor, Hirsch index = 18; participation in over 20 international conferences and workshops; Co-Director of a NATO Advanced Study Institute.

On February 20, 2008 Assoc. Prof. Valentin Popov, a lecturer at Physical Faculty of Sofia University St. Kliment Ohridski, got an award "For particular contribution to science" for young scientist for achievements in the field of theoretical investigation and computer modeling of physical properties of carbon nanotubes.

His scientific investigations encompass theoretical modeling and computer simulations of fundamental physical properties of new materials. Part of his work focuses on the calculation of the lattice dynamics of metallic oxides with application of the obtained results for the assignment of observed lines in the Raman spectra of these compounds to definite phonons. Second equally large part of the study is connected with fullerenes, fullerides, and carbons and boron-nitride nanotubes. For the nanotubes, a symmetry-adapted approach to the lattice dynamics and the electronic band structure is proposed and illustrated with calculations in the framework of a phenomenological model and a tight-binding model. The obtained results reveal for the first time the characteristic dependence of the phonons and electrons on the nanotube type. As a continuation of this line of research, calculation of a large number of mechanical, thermal, dielectric, and optical properties was performed for several hundred nanotube types. The collected data form a basis for further modeling and computer simulations of the properties of specific nanotube systems that could find future industrial application.

Mr. Valentin Popov has graduated from the University of Sofia, Faculty of Physics. He defends his MSc degree in 1980, PhD thesis "Lattice dynamics of high-Tc superconductors" in 1995 and his DSc thesis: "Electronic and vibrational properties of carbon nanotubes" in 2007.

Research experience of Mr. V. Popov includes:

• 1995-1996: "Post-doctoral research on the theory of the anharmonic broadening and frequency shift of the Raman lines due to optical phonons in GaAs/AlAs superlattices" in Laboratoire de Physique des Solides, Université Pierre et Marie Curie, Paris, France

Funding: Boursier de thèse - Réseau "formation-recherche" EST - Ministère de l'Education nationale de l'Enseignment supérieur et de la Recherche (France)

• 1997-2003: "Dynamical, elastic, thermal and optical properties of carbon nanotubes (single-walled and multi-walled) and bundles of nanotubes (finite and infinite) within phenomenological, tight-binding and ab-initio approaches" in Department of Physics, University of Antwerp (RUCA), Antwerp, Belgium

Funding: NATO Collaborative Research Grant, NATO Senior Research Fellowship, Flemish Concerted Action, Fund for Scientific Research Flanders (FWO), Visiting Professor at UA (RAFO)

• 2004-2006: "Vibrational and electronic properties of nanotube systems" in Laboratoire de Physique du Solide, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Funding: NATO Collaborative Linkage Grant, NATO Advanced Study Institute Grant, Research Fellowship from the Federal Science Policy Office of Belgium, NATO Collaborative Linkage Grant, Marie-Curie Intra-European Fellowship

• 2006- "Physical properties of nanotubes" in Faculty of Physics, University of Sofia

Funding: NATO Collaborative Linkage Grant, Marie-Curie Reintegration Grant

Professional experience of Mr. V. Popov includes the following positions:

• 1981: Assistant, Institute for Foreign Students;

• 1989: Research Collaborator III deg.;

• 1995: Principal Assistant;

• 2000: Associate Professor, Faculty of Physics, University of Sofia.

Mr. V. Popov has a rich teaching experience in seminars in the field of: Programming and Numerical Methods, Complex Analysis, Ordinary Differential Equations, Theoretical Mechanics, Mechanics of Fluids, Thermodynamics and Statistical Physics, Electrodynamics; and lectures in: Vector and Tensor Analysis, Theoretical Mechanics, Thermodynamics and Statistical Physics, Electrodynamics, Quantum Mechanics, Theory of the Solid State.

Assoc. Prof. DIANA NESHEVA, PhD

Institute of Solid State Physics, Bulgarian Academy of Sciences

Phone: +359 2 9795000 226; Fax: +359 2 9753632

E-mail: nesheva@issp.bas.bg

Author and co-author of 110 original papers; Head of the laboratory "Photoelectrical and optical phenomena in wide gap semiconductors" and of the "Nanophysics" department; Member of the Scientific Council of the Institute.

Diana Nesheva graduated from Sofia University, Bulgaria in 1976. In 1982 she obtained her PhD degree in "Creation and investigation of some photoinduced phenomena in CdS" from the Institute of Solid State Physics of Bulgarian Academy of Sciences. Afterwards she carried out studies on inorganic amorphous and crystalline materials such as chalcogenide glasses and thin films, a-CdS, a-Si:H and a-$Si_{1-x}Ge_x$:H thin films, photorefractive $Bi_{12}SiO_{20}$ crystals, etc. She has great experience in vacuum techniques for preparation of semiconductor thin films as well as in electrical, photoelectrical and optical characterization of crystalline and amorphous semiconductors.

Subjects of her recent interest are two-component systems including low-dimensional inorganic semiconductor materials (multilayers and superlattices from amorphous and nanocrystalline materials as well as semiconductor nanoparticles embedded in various matrices). Studies on these systems are concentrated on size-induced effects in the electron and phonon subsystems, structure and structural stability, transport mechanisms, etc. X-ray diffraction, high-resolution electron microscopy, Raman scattering, photoluminescence, absorption and electrical measurements are carried out.

Very recently the studies on the nanostructured thin films have been directed to development of gas-sensors. The research in this field has been partially supported under a NATO linkage grant (CLG 980656) entitled "Optoelectronic properties of semiconductor thin films for gas sensor applications".

Diana Nesheva is the author and co-author of 110 original papers, most of which are published in representative International Journals such as Phys.Rev.B, J. Appl. Phys., Philosophical Magazine B, J. Non-Crystalline Solids, etc. She has been supervisor of 4 undergraduate and 3 postgraduate students.

She is head of the laboratory "Photoelectrical and optical phenomena in wide gap semiconductors" and of the "Nanophysics" department at the Institute of Solid State Physics of BAS. Also, she is a member of the Scientific Council of the Institute. The staff of the laboratory is able to fabricate nanostructured thin films including semiconductor materials with physical evaporation in high vacuum. Set-ups for electrical, photoelectrical and optical measurements are also available in the laboratory.

Co-operative studies on low-dimensional system have been carried out with:

• Dundee University, Dundee, Scotland;

• Institute of Physics, Carl von Ossietzky University Oldenburg, D-26111 Oldenburg, Germany;

• National Polytechnical University of Athens, Greece;

• Max-Planck-Institut, Halle, Germany;

• Institute of Physics, Center for Solid State Physics and New materials, Belgrade, Serbia&-Montenegro.

Assoc. Prof. ANA PROYKOVA, PhD
University of Sofia, Faculty of Physics
Phone: (+359)-2-8161 828; Fax: (+359)-2- 8622546
E-mail: anap@phys.uni-sofia.bg

Many publications in peer-reviewed Bulgarian and international journals; participation in International Conferences and Meetings, Reports on research and educational projects.

Assoc. Prof. Dr. Ana Proykova has graduated from the University of Sofia. She defends her MSc degree in 1974. In 1981 she defends PhD in Physics in University of Sofia and JINR, Dubna.

The work experience of Mrs. Ana Proykova includes:

Current positions:

• Head, Monte Carlo Group (lab Modeling of physical processes), University of Sofia;

• Vice-President, National Expert Council on Nanotechnologies, Bulgarian Academy of Sciences (NECNT-BAS) (2005 – at present);

• Program Committee Member, NanoMatPro FP7 (2007 - at present);

• National delegate to the ESFRI-EU (Sep., 2007 up to now);

• Bulgarian representative in the Member States Council on the international dialogue on responsible research and development of nanotechnologies.

Concurrent Positions:

1999-2003: Vice-dean, Faculty of Physics, University of Sofia;

2002-2006: National Contact Point (NCP) - Thematic Priority 'NanoMatPro', FP6 – EC;

1998 (summer semester): Visiting Scholar at the Institute for Nuclear Theory, University of Washington, USA;

1997 (spring): Invited Professor at the Catholic University of Louvain (UCL), Belgium;

1995 (January-October): **Fulbright Senior Scholar** at the University of Chicago, USA.

Professional Occupations:

• Member of the Program Committee of the NanoMatPro, EU-FP6 (2004- 2006);

• Member, National Scientific Commissions: Physics (2002-2004), Nanotechnology (2003 – at present), Ministry of Education and Science;

• Member, Council Board for the Research at the Universities (Ministry of Education and Science) (2003- at present);

• Member, Advisory Board for International Education and Cultural Exchange Programs, Ministry of Education and Science (2001-2004).

Professional Service:

• Chair of the chapters "Clusters and Nanoparticles" (2000-2004) & "Theory, Modeling, Simulation", National Centre on NanoTechnology, (2005 -);

• Member, Executive Board of the Union of Physicists in Bulgaria (2001-2004);

• Team leader IUPAP Working Group on Women in Physics;

• Referee of Scientific Papers for *Computer Physics Communications, Journal of Chemical Physics, Internet Journal of Molecular Science.*

Editorship, Editorial Boards:

• Editor of the *International Journal of Molecular Science,* http://www.ijms.org/;

• Guest-editor for the special issue of IJMS devoted to the 70'th anniversary of RS Berry, http://www.mdpi.org/ijms/papers/i3010001.pdf;

• Founder and Editor of the annual proceedings "Meetings in Physics @ University of Sofia" (since 1999). Published by Heron Press (Scientific Series) Sofia;

• Editor, Atomic and Molecular Physics, *Central European Journal of Physics* (2006 - at present).

Mrs. Ana Proykova has professional visits and has worked at many other international universities. She has teaching experience in Atomic and Nuclear Physics (ANP), Computational and Theoretical Condensed Matter Physics; Cluster Physics; Statistical Physics and its Applications.

Her research activities include: Finite-size systems; molecular and atomic clusters; low-dimensional discrete systems; self-organization, nanotubes and their properties, Monte Carlo simulations, Molecular Dynamics Method, Density functional theory.

Current Research Projects:

• Carbon Nanotubes – mechanical and electrical properties (Prof. Jeff Gordon, Israel & Hui Tong Chua, Singapore & Feng-Yin Li, Taiwan & I. Dragieva, BAS, Bulgaria) Funding: Taiwan & Ministry of Education and Science (BG);

• "Adsorption of simple gases on/in carbon nanotubes" Funding: HPC-Europe, FP6;

• *Ab initio* calculations of methane adsorption on carbon nanotubes with defects Funding: NSF-Bulgaria & SU Scientific Fund;

• Optimization of Cluster Configurations (genetic algorithm) Funding: SU Scientific Fund;

• Chromium clusters in magnetic field Funding: SU Scientific Fund.

Current Funded Projects in science & society activities:

• COOREERS, CA- FP6, NanoMatPro TP3 (Nanoscience, materials, production);

• Nanoforum, European Union sponsored Thematic Network – FP5, http://www.nanoforum.org;

• Platform of Women in Science, SSA-FP6–Science and society, http://www.epws.org/.

Selected Completed Research Projects in collaboration 2000–2006:

- Econophysics & Sociophysics (with Prof. D. Stauffer, University of Cologne) Funding: University of Cologne-University of Sofia partnership;

- Molecular and Atomic Clusters, Phase Transitions in Small Systems (The University of Chicago, USA with Prof. RS Berry) Funding: NSF-USA (2002-2006);

- Magnetic chromium clusters (with Prof. D. Stauffer, University of Cologne) Funding: University of Cologne - University of Sofia partnership (2004-2005);

- *Ab initio* calculations of metal clusters (DFT - code, J. Chelikowski, Minnesota Supercomputing Center, USA, 2001-2004);

- Finite-Size Scaling Analysis (NATO CLG project with R.S. Berry: 2000-2002);

- Hydrogen Bond Network & Clatrates (with Prof. Ohmine, Univ. of Nagoya, Japan, 2000);

- Potential Energy Surface (PES) Analysis of Clusters (JSPS project, Japan: 2000).

Awards and personal grants: Diploma for outstanding performance and lasting contribution (2002), European Community (1993), Fulbright Senior Scholar (1995),TEMPUS (1997), JSPS (1999), NATO CLG (2001), Visiting Scientists Grant (Israel, 2002), Research Scientists Exchange Program Singapore-Bulgaria (2003).

AWARDS

BADGE OF HONOUR FOR CONTRIBUTION TO EUROPEAN EDUCATIONAL PROGRAMS IN BULGARIA

Since 2007 the Human Resources Development Center has established a Golden Badge of Honour for merits to European educational programs in Bulgaria. The initiative has for its goal to distinguish politically responsible persons, experts, participants in the programs who have contributed to their successful realization in Bulgaria.

Daniel Valchev, Deputy Prime Minister and Minister of Education and Science, Veselin Metodiev, Minister of the Ministry of Education and Science (1997-1999), Ivan Neikov, Minister of Labour and Social Policy (1997-2001), Prof. Kamen Velev, Deputy Minister of Education and Science (2003-2005) and Vasil Gadev, Headmaster of Sofia Professional High School of Tourism – beneficiary of "Leonardo da Vinci" and "Komenski" programs – are among those distinguished with a Golden Badge of Honour for the year 2007. Bulgarian National Television, "24 Hours" newspaper and Radio France Internationale" also received Golden Badge of Honour in 2007.

THREE UNIVERSITIES ARE AWARDED FOR ACHIEVEMENTS IN THE FIELD OF INFORMATION TECHNOLOGIES

Three university projects were awarded for exceptional achievements in the sphere of information and communication technologies at the official ceremony within the framework of the sixth edition of Scientific-Educational "Expo 2007". It was held within the framework of the International Technical Fair in Plovdiv. Organizers of the event are: ICT Media, State Agency for Information Technologies and Communications, United Nations Development Program (UNDP) and Youth Innovation and Information Society AB.

Twelve projects from 10 higher educational institutions, chosen by criteria of innovativeness and practical applicability, reached the finals of the competition.

The selection committee adjudged the following distinctions:

Grand Prize – to American University in Bulgaria, "Computer Sciences" Department, for a system of access to digital and analogue information resources "Library Link Resolver";

Second Prize – to Technical University - Sofia, "Computer Systems" Department, for virtual screening and computer modeling of design of pharmaceuticals;

Third Prize – to Technical University - Varna, "Computer Sciences and Technologies" Department, for a system of speech presentation of graphical images.

First Encouraging Prize was bestowed on the team of State Institute of Library Studies and Information Technologies and its integrated library-information RFID system for automation of activities in the Library-Information Center at SILSIT.

Second Supporting Prize was bestowed to the team of the Mathematics and Informatics faculty of Sofia University "Kliment Okhridski" for the project "Creation of a product working with cogitative cards, with the aim to be used in education of schoolchildren, students and teachers (Bookvar)".

Third Encouraging Diploma was received by Plovdiv University "Paisii Hilendarski" for an interdisciplinary project "Modern methods, means and technologies in diagnostics, consulting and educating persons with disabilities", developed together with faculties of pedagogics and information technologies of the university.

"Microsoft Bulgaria" adjudged Special awards in order to promote and stimulate innovative activities in the field of information and communication technologies and applicability of research projects in practice.

"EUREKA" FOUNDATION AWARDS FOR THE YEAR 2007

On January 16, 2008 official bestowal of "Eureka" awards to prize-winners for the year 2007 for achievements in science, young manager and young farmer took place in Sofia.

The awards are adjudged to young people for their significant achievements in science, for inventions with great public importance, for achievements in management of business organizations as well as for the highest results in development of agricultural activities.

"EUREKA" award for achievements in science was bestowed to **Neli Danchova Bundaleska** from the Institute of Solid State Physics at the Bulgarian Academy of Sciences /BAS. Neli Bundaleska starts her professional career in 1999 as a physicist at the Central Laboratory of Photoprocesses "Acad. J. Malinovski" of BAS, and since 2002 she has been a regular PhD student at the Department of Atomic Spectroscopy of the Institute of Solid State Physics at BAS.

She is an author of 15 scientific publications and papers at national and international conferences. She took part in projects of the National Council "Scientific Research" at the Ministry of Education and Science and Nuclear Reactions Laboratory at the Joint Institute for Nuclear Research in Dubna, Russia. Her research interests are in the field of laser and plasma physics, glow discharge and discharging processes in a hollow cathode; elementary processes in plasma. She is a member of the Union of Physicists in Bulgaria and SPIE – The International Society for Optical Engineering.

Neli Bundaleska gets joint award of "EUREKA" Foundation and the Supreme Certifying Commission at the Council of Ministers for defended dissertation on the topic: "Polarizational optogalvanic spectroscopy of a discharge in a hollow cathode" in which the author makes interpretation of experimental results on the basis of existing theoretical models.

"EUREKA" award for young manager for the year 2007 was adjudged to **Peter Tzvetanov Dudolenski –** manager of RESB LLC, for successful realization of business projects and investments in trade entertainment centers, for active participation in.

EUREKA" award for young farmer for the year 2007 was adjudged to **Mikhail Simeonov Minchev** from the city of Svishtov for highest results and successful realization of agricultural activities in conformity with European requirements.

Boris Todorov Radulov – vice executive manager of "Fibran" Joint-stock Co. and **Nikola Vaskov Vasilev** – head manager of "Saturn Engineering" LLC, were awarded an **honorary diploma** for excellent presentation in the competition.

In the competition among young farmers **Hristo Borisov Tzvetanov** – agricultural producer from Svishtov, **Silvia Ruso** – agricultural producer from Pazardzhik, **Dimitar Ivanov Avramov** – agricultural producer from Montana, were awarded a **diploma** for excellent presentation.

ARTICLES

RECENT PUBLICATIONS OF BULGARIAN SCIENTISTS

Title: **Early time ripening during the growth of CdSe *nanocrystals* in liquid paraffin.**

Authors: Yordanov, Georgi G.[1], Dushkin, Ceco D.[1] nhtd@wmail.chem.uni-sofia.bg, Adachi, Eiki[2]

Source: Colloids & Surfaces A: Phys. Eng. Asp., Vol. 316, 1-3, (Mar. 2008), 37-45

Document Type: Article

Author Affiliations: [1]Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria; [2]Advanced Research Centre, Nihon L'Oreal R&D Centre, 3-2-1 Sakado, Takatsu, Kawasaki, Kanagawa 213-0012, Japan.

ISSN: 0927-7757

Title: **Development of bioadhesive amino-pegylated poly(anhydride) *nanoparticles* designed for oral DNA delivery.**

Authors: Yoncheva, Krassimira[1], Centelles, Miguel N.[2], Irache, Juan M.[2]

Source: Journal of Microencapsulation, Vol. 25, 2, (Mar. 2008), 82-89

Document Type: Article

Author Affiliations: [1]Department of Pharmacy and Pharmaceutical Technology, University of Navarra, Pamplona, Spain; Department of Pharmaceutical Technology, Faculty of Pharmacy, Sofia, Bulgaria;
[2]Department of Pharmacy and Pharmaceutical Technology, University of Navarra, Pamplona, Spain.

ISSN: 0265-2048

Title: ***Nanocomposites* of isotactic polypropylene with carbon *nanoparticles* exhibiting enhanced stiffness, thermal stability and gas barrier properties.**

Authors: Vassiliou, A.[1], Bikiaris, D.[1] dbic@chem.auth.gr, Chrissafis, K.[2], Paraskevopoulos, K.M.[2], Stavrev, S.Y.[3], Docoslis, A.[4]

Source: Composites Science & Technology, Vol. 68, 3/4, (Mar. 2008), 933-943

Document Type: Article

Author Affiliations: [1]Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece;
[2]Solid State Physics Section, Physics Department, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece;
[3]Bulgarian Academy of Sciences, Space Research Institute, Department of Space Materials and Nanotechnologies, 6 Moskovska Street, Sofia, Bulgaria;
[4]Department of Chemical Engineering, Queen's University at Kingston, Kingston, ON, Canada K7L 3N6.

ISSN: 0266-3538

Title: **Mesoporous and nanostructured CeO2 as supports of nano-sized gold catalysts for low-temperature water-gas shift reaction.**

Authors: Yuan, Zhong-Yong[1,2] zyyuan@nankai.edu.cn, Idakiev, Vasko[3] idakiev@ic.bas.bg, Vantomme, Aurélien[1], Tabakova, Tatyana[3], Ren, Tie-Zhen[4], Su, Bao-Lian[1] bao-lian.su@fundp.ac.be

Source: Catalysis Today, Vol. 131, 1-4, (Feb. 2008), 203-210

Document Type: Article
Author Affiliations: [1]Laboratory of Inorganic Materials Chemistry, The University of Namur (FUNDP), 61 rue de Bruxelles, B-5000 Namur, Belgium;
[2]Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Tianjin 300071, PR China;
[3]Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, bl. 11, 1113 Sofia, Bulgaria;
[4]Structural Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691 Stockholm, Sweden.
ISSN: 0920-5861

Title: **Effect of compatibilizer and electron irradiation on free-volume and microhardness of syndiotactic polypropylene/clay *nanocomposites*.**
Authors: Misheva, M.[1], Djourelov, N.[2] nikdjour@inrne.bas.bg, Zamfirova, G.[3], Gaydarov, V.[4], Cerrada, M.L.[4], Rodrнguez-Amor, V.[4], Pérez, E.[4]
Source: Radiation Physics & Chemistry, Vol. 77, 2, (Feb. 2008), 138-145
Document Type: Article
Author Affiliations: [1]Faculty of Physics, Sofia University "Kl. Ohridsky", J. Bourchier Blvd. 5, 1126 Sofia, Bulgaria;
[2]Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72 Tzarigradsko shoosse Blvd., 1784 Sofia, Bulgaria;
[3]Higher School of Transport "T. Kableshkov", Geo Milev str. 159, 1574 Sofia, Bulgaria;
[4]Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006-Madrid, Spain.
ISSN: 0969-806X

Title: **Electrochemical hydriding/dehydriding of nanocrystalline Mg2-xSnxNi (x = 0, 0.1, 0.3).**
Authors: Drenchev, Nikola[1], Spassov, Tony[1] tspassov@chem.uni-sofia.bg, Kanazirski, Ivan[2]
Source: Journal of Applied Electrochemistry, Vol. 38, 2, (Feb. 2008), 197-202
Document Type: Article
Author Affiliations: [1]Department of Chemistry, University of Sofia "St. Kl. Ohridski," 1, J. Bourchier str., Sofia 1164, Bulgaria;
[2]University of Chemical Technology and Metallurgy, Sofia, Bulgaria.
ISSN: 0021-891X

Title: **Core losses in nanocrystalline soft magnetic materials under square voltage waveforms**
Authors: Valchev, Vencislav[1], Van den Bossche, Alex[2], Sergeant, Peter[2]
Source: Journal of Magnetism and Magnetic Materials, Vol. 320, 1-2, (2008), 53-57
Document Type: Article
Author Affiliations: [1]Tech Univ Varna, Varna, Bulgaria;
[2]Univ Ghent, Sint Pietersnieuwstr 41, Ghent, Belgium.
ISSN: 0304-8853

Title: **Electrochemical growth of single copper crystals on glassy carbon and tungsten substrates**
Authors: Zapryanova T., Jordanov N., Milchev A
Source: Journal of Electroanalytical Chemistry, Vol. 612, 1, (Jan. 2008), 47-52

Document Type: Journal Paper
Author Affiliations: Bulgarian Acad. of Sci., Sofia, Bulgaria
ISSN: 0022-0728

Title: **Investigation on functional and reliability properties of IR heaters for soldering processes in connection with spectral characteristics of radiation control**
Authors: Kontrov S., Marinova M., Mashkov P., Pencheva T.
Source: 29th International Spring Seminar on Electronics Technology Nano Technologies for Electronics Packaging. IEEE. pp. 197-201. Piscataway, NJ, USA.
Document Type: Conference Paper
Author Affiliations: Technical University, Varna, Bulgaria.
ISBN: 1-4244-0550-5

NEW DISSERTATIONS ON THE SUBJECT: "NANOTECHNOLOGIES AND NANOMATERIALS" "SIRENA" Database – NACID

Author Spassov, Tony Georgiev
Degree DSc
Title Nanocrystalline metallic alloys: synthesis, microstructure and properties
Affiliated Organization Sofia University "St. Kliment Okhridski", 15, Tsar Osvoboditel Blvd., 1504 Sofia
Abstract The doctoral thesis is devoted to preparation of homogeneous nanocrystalline alloys of different type ("metal-nonmetal", "metal-transition metal", "transition metal-transition metal"; based on Fe, Ni, Zr, Ti, Mg) by means of rapid solidification from the melt, mechanical alloying and controlled crystallization of amorphous precursors with improved magnetic, chemical and mechanical properties. Experimental parameters of different approaches and methods for synthesis of nanocrystalline alloys with definite microstructure and properties are optimized. Experimental conditions for realization of controlled crystallization, the reasons for the formation of nanocrystalline phases as well as the thermal stability of the nanocrystalline materials produced are investigated, too. Important information about some magnetic, mechanical and chemical properties of these new materials is obtained, as the properties are compared with those of the amorphous and polycrystalline materials. The studies carried out in the doctoral work complement and extend the knowledge about the relationship between the microstructure and properties of nanocrystalline materials, which is essential for the design of new materials with properties exceeding those of the conventional materials.
Depositary Library Central Research and Technical Library

Author Velichkova, Kalinka Hristova
Degree PhD
Title Modification of polymers by creation of nanoformations by means of ion implantation and subsequent gamma irradiation
Affiliated Organization Institute of Nuclear Research and Nuclear Energetics (BAS), 72, Tsarigradsko shose Blvd., 1784 Sofia
Abstract Three structurally different polymer dielectrics, namely ultrahigh molecular weight polyethylene (UHMWPE), polypropylene (PP) and polymethylmetacrylate (PMMA) were implanted by 30 keV energy carbon ions (C^+) at doses in the interval $5x10^{12}$ cm^{-2} - $2x10^{17}$ cm^{-2} or by 90 keV energy selenium ions (Se^+) at doses

from $2.5x10^{16}$ cm^{-2} to $1.5x10^{17}$ cm^{-2}. The carbon implanted polymers were irradiated after that with gamma rays at doses from 0.1 to 3 Mrad accumulated in steps. In dependence on the implantation dose the surface conductivity (σ_S) was showing an increase of up to 9 orders in magnitude. The gamma processing caused changes in σ_S, whose direction and magnitude were dependent on the polymer type and both on the implantation and irradiation doses. The increase of the implantation or irradiation doses was followed by a drop in the activation energy. The activation energy became negative at about $l\text{-}2x10^{17}$ cm^{-2} and 1.5-3 Mrad. These changes were explained by carbon nanoformation created during the process of ion implantation and after it. The gamma irradiation helps the build up of carbon chains at lower implantation doses and breaks the built chains down at the higher implantation doses. Similar changes in σ_S were observed also for the polymers implanted by Se^+. It was established that the charge transport mechanism that was describing best the experimental results was depending on the polymer type, the implantation dose, the temperature interval and the measuring regime. The aging of PMMA implanted by Se^+ ions was accompanied with lessening of σ_S most strongly at the highest implantation dose and with changes of the charge transport mechanism due to creation of carbon and selenium nanoformations during the ion implantation process and their destruction with time. UHMWPE and UHMWPEC (composite of UHMWPE and silenite ($Bi_{12}SiO_{20}$)) both implanted by C^+ possess photoluminescence and the best conditions for it are at implantation dose of $5x10^{14}$ cm^{-2}. The photoluminescence emission was possible to deconvolute into spectral regions, wherein there is the emission of different in arrangement, structure and size carbon formations, the silenite and the polymer UHMWPE itself. The changes in the optical properties of implanted polymers, similarly to their electrical properties were connected with the carbon and selenium nanoformations, clusters, aggregates and cluster chains created during the ion implantation process. A change in the free volume distribution for the implanted polymer and subsequently gamma irradiated implanted polymer was established by means of positron annihilation spectroscopy using slow positrons. The effect was connected with a process of crosslinking and release of the low molecular fragments and hydrogen under the action of ionizing (photonic and corpuscular) irradiation upon the material.

Depositary Library Central Research and Technical Library

Author Minkov, Ivan Lyubomirov
Degree PhD
Title Behaviour of lipid nanostructures - nanocapsules and alveolar surfactants at air/ water interface
Affiliated Organization Sofia University "St. Kliment Okhridski", 15, Tsar Osvoboditel Blvd., 1504 Sofia
Abstract Dispersions of particles with size under one micrometer are an interesting object for scientific investigations and applications as biodegradable drugs carriers as well as alveolar surfactant preparations. In the present thesis the behaviour of water/air interface of a new class of lipid nanocapsules (LNC) with possible applications in the medicine, as well as five pulmonary surfactant preparations, used in the clinical practice, are investigated. A kinetic model describing the destruction of the unstable fraction nanocapsules (LNC I) and the formation of monolayer at the air/water interface is developed. The correspondig kinetic constants are estimated. The state, electrical and rheological characteristics of the monolayers formed from LNC and alveolar surfactants - dilatational elasticity

and characteristic times of relaxation are estimated. The action of the hydrolytic enzymes Humicola lanuginosa lipase (HLL) and pancreatic phospholipase A_2 (PLA_2) on monolayers formed from lipid nanocapsules (LNC) and model monolayers containing their components (Labrafac, Solutol and Lipoid) is studied. Kinetic models describing the hydrolysis with the enzyme HLL of monolayers from Labrafac, Solutol and mixtures Labrafac/Solutol are developed. The values of the global kinetic constants, which characterize the process of hydrolysis, are found. A morphological study of the monolayers formed from the pulmonary surfactants by using atomic force microscope (AFM) is done.

Depositary Library Central Research and Technical Library

Author Kolev, Svetoslav Mihaylov

Degree PhD

Title Magnetic and microwave properties of nanostructured ferroxides with low and high magneto-crystalline anisotropy (magnetite, Fe_3O_4) and high (barium hexaferrites, $BaFe_{12}O_{19}$)

Affiliated Organization Institute of Electronics (BAS), 72, Tsarigradsko shose Blvd., 1784 Sofia

Abstract The dissertation work deals with the magnetic and microwave properties of nanostructured magnetic ferroxides with low (magnetite, Fe_3O_4 and high (barium hexaferrite, $BaFe_{12}O_{19}$) magneto-crystalline anisotropy in view of their application as absorbing structures in the microwave range. The nanostructured particles studied were with size 10, 30, 300, 3000 nm (Fe_3O_4) and 80 and 500 nm ($BaFe_{12}O_{19}$). The analysis of the data obtained by ILEEMS Moessbauer spectroscopy demonstrated the existence of a defective structure to a depth of 3 nm from the surface of the Fe_3O_4 particles, which we determined as being quasi γ-Fe_3O_4. The deviations observed in the crystalline structure on the Fe_3O_4 particle surface point to the complexity of the magnetic interactions there and cannot be explained by the unordered state of the surface magnetic moments only (Kodama-Berkowitz theoretical model). We relate the anomalies observed to the presence of an effective magneto-crystalline anisotropy, which determines the nanoparticle's magnetic properties and combines the effects of the magneto-crystalline, exchange, surface, and shape anisotropies. This is especially clearly observed in particles with high magnetic anisotropy ($BaFe_{12}O_{19}$), which retain their specific shape even below 100 nm. Measurements at high magnetic fields are especially suited to revealing such effects. The Moessbauer spectroscopy studies showed that the filling of the magnetic sublattices in the crystal cell of a nanosized particle differs from that of the well-crystallized edged particle. In the case of $BaFe_{12}O_{19}$ the intermediate Ba-containing block exhibits the largest deviations in the filling of the low-symmetry vacancies - trigonal bipyramidal and tetrahedral sites. Further, we studied the microwave properties of composite materials based on a polymer matrix containing dispersed Fe_3O_4 with particles size 30, 300, 3000 nm. In the case of nanosized filler we found that the ferromagnetic resonance frequency is shifted to the short wavelength region, as compared with conventional (micron-sized) fillers, which we relate to the increase in the effective anisotropy field intensity due to the surface effects in the nanosized particle. Our results demonstrate the possibility to vary the resonance properties of these materials in a controlled way by means of varying the filler particles size.

Depositary Library Central Library of Bulgarian Academy of Sciences

EVENTS

2–4 May 2008
The 9th **WSEAS** International Conference on
Neural Networks (NN'08)
Sofia, Bulgaria
Address:
E-mail: *info@wseas.org*
Web site: *http://www.wseas.org/conferences/2008/sofia/nn/index.html*

2–4 May 2008
The 9th **WSEAS** International Conference on
Fuzzy Systems (FS'08)
Sofia, Bulgaria
Address:
E-mail: *info@wseas.org*
Web site: *http://www.wseas.org/conferences/2008/sofia/fs/index.html*

2–4 May 2008
The 9th **WSEAS** International Conference on
Evolutionary Computing (EC'08)
Sofia, Bulgaria
Address:
E-mail: *info@wseas.org*
Web site: *http://www.wseas.org/conferences/2008/sofia/ec/index.html*

3 June 2008
International Conference
IDC's Storage, Virtualization and Green Data Centers Roadshow 2008
Virtual Changes, Real Savings, Brighter Future
Sofia, Bulgaria
Address:
IDC Bulgaria
WTC Interpred, Office 333
36, Dragan Tzankov Blvd., 1040 Sofia, Bulgaria
Phone/Fax: (+359) 2 969 30 56
Web site: *www.idc-cema.com*

9–13 June 2008
17th International Symposium
ECOLOGY & SAFETY
Sunny Beach resort, Bulgaria
Address:
Info Invest Ltd – Bulgaria
Phone: (+359) 56 950077
Mob. Phone: (+359) 878 844410
E-mail: *office@sciencebg.net; symposium@sciencebg.net*

16–20 June 2008
VIII International Scientific Conference **SGEM**
Modern Management of Mine Producing, Geology and Environmental Protection
Albena Complex, Bulgaria
Address:
14, "Kliment Ohridsky" Blvd.
1797 Sofia, Bulgaria
Phones: (+359) 2 975 3982; (+359) 2 817 2434
Fax: (+359) 2 817 2477
E-mails: *sgem@sgem.org; sgem@stef92.com*
Web site: *www.sgem.org*

26–28 June 2008
International Scientific Conference
Informatics in the Scientific Knowledge 2008
ISK'2008
Varna, Bulgaria
Address:
VFU "Chernorizets Hrabar",
Department of Informatics
9007 Varna, к.к. Chaika
Phone: (+359) 52 359 572
Fax: (+359) 52 359 573
E-mail: *ISK2008@vfu.bg*

16–22 June 2008
International Conference
"Knowledge–Dialogue–Solutions" (KDS–2008)
Varna, Bulgaria
Address:
E-mail: *foi@nlcv.net*
Web site: *www.foibg.com*

23 June – 03 July 2008
International Conference
"Information Research and Applications" (i.TECH–2008)
Varna, Bulgaria
Address:
E-mail: *info@foibg.com*
Web site: *www.foibg.com*

23 June – 03 July 2008
International Conference
"Modern (e–) Learning" (MeL–2008)
Varna, Bulgaria
Address:
E-mail: *info@foibg.com*
Web site: *www.foibg.com*

NOTES