V4–Japan Joint Research Program

FINAL REPORT

Name of the project:	Nanophotonics with Metal - Group-IV-Semiconductor Nanocomposites: From Single Nanoobjects to Functional Ensembles (NaMSeN)
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Date: January 1, 2016 – December 31, 2018

Executive Summary of the NamSeN consortium

The NaMSeN project covered broad range of activities from synthesis of nanoparticles (Si – pure and doped, SiC, Au nanorods), their detailed characterization using the most advanced methods (like atom probe tomography) to fabrication of complex nanocomposites and MOS/MIS devices (for memory devices). The project included cutting edge theoretical modelling, taking advantage especially from combined expertise in quantum Monte-Carlo and density functional theory (DFT). Fabricated materials were tested for their bio-compatibility in cell cultures; nanoparticles were imaged and tracked in cells using the most advanced fluorescence and spectroscopy techniques (single nanoparticle luminescence spectroscopy, etc.) and the crucial role of the protein-corona covering particles in biological medium was studied. The nanocomposites of semiconductor nanoparticles with noble-metal (Au, Ag, Pt) structures enabled increase of both the absorption cross section and the radiative rate - this is important step towards their potential application in nanophotonics or bio-imaging. The results were published in 46 papers so far. During the course of the project we organized six workshops and one three-day symposium, many student and young researchers exchange stays, which created conditions for sustainable international collaboration between the participating groups.

FINAL REPORT

Wigner Research Centre for Physics, Hungarian Academy of Sciences (Work Package 3), Ádám Gali's Semiconductor Nanostructures Research Group

Work plan and deviations from the plan

The ultimate goal of this international project was to create and foster sustainable scientific collaboration between participants in the Visegrad 4 (V4) countries and Japan. The work was organized in five work-packages (WP) one per participating organization where WP 3 listed the tasks for the partner of Wigner Research Centre for Physics. The original work plan of WP 3 was to calculate the optical properties of pristine, heavily doped and alloyed Si nanoparticles (Si NPs), including surface effects by means of time-dependent density functional theory (TD DFT). The corresponding Si NPs were prepared in Professor Minoru Fujii group at Kobe University. In the original work plan the Si nanoparticles would have been alloyed by germanium with considerable spin-orbit interaction. Instead, the research consortium considered silicon carbide nanoparticles (SiC NPs) that were prepared and developed at Wigner Advanced Materials Integrated Laboratory (ADMIL) by Ádám Gali's research group. As a consequence, ***the role of Wigner Research Centre for Physics in the V4+Japan consortium was extended by preparation and analysis of SiC NPs that led to further deepening the tight collaboration of the consortium partners.***

Scientific results

The work of Ádám Gali's research group can be divided into two main thrusts: (i) DFT and TD DFT studies of Si and SiC NPs, in order to understand their vibration and optical properties, and identify the dopant configurations in Si NPs and the effect of surface termination of Si and SiC NPs; (ii) prepare and analyze SiC NPs, in particular, in the aspect of bioimaging applications.

(i) Atomistic *ab initio* studies

Most of the results are summarized as thesis points as they were published in long scientific papers. It is emphasized that these long papers summarize more than a year effort in each case. All the scientific articles contain very detailed and thorough studies where two of them were joint cooperation with the Ivan Štich group at the Slovak Academy of Sciences. The most recent results on the effect of surface on the optical properties of Si NPs are summarized here in details that will be published in a forthcoming scientific paper.

(a) Our paper entitled "Optical Gaps in Pristine and Heavily Doped Silicon Nanocrystals: DFT versus Quantum Monte Carlo Benchmarks" was published in the Journal of Chemical Theory and Computation, and contains a detailed benchmark evaluation of various common and less common exchange-correlation functionals. While DFT is the main workhorse of atomistic computer simulations, it's main limitation that the exact exchange-correlation functional can be only approximated. This limits the accuracy and reliability of DFT-based methods. Often some approximate functionals provide good results for certain sets of systems while give quantitatively and qualitatively incorrect results for different systems. In this study, our goal was to evaluate most of the common exchange-correlation functionals in terms of their ability to predict the optical properties of small, co-doped silicon nanoparticles (Si NPs). We compared the excitation energies obtained by adiabatic TD DFT calculations utilizing semi-local, hybrid and range-separated hybrid functionals with vertical excitation energies obtained utilizing Quantum Monte Carlo (QMC) methods. The QMC calculations were carried out by Prof. Ivan Štich's group (Slovak Academy of Sciences) who is an expert on QMC methods. Due to the severe computational cost of the QMC method, only small (<50 atoms) Si NPs were studied. We found that most common exchange-correlation functionals underestimate the optical gap. In addition, we also found that the DFT-Koopmans' theorem can be also utilized to predict the accuracy of exchange-correlation functionals. The insights gained from this study are expected to be useful for future simulation studies of molecule sized semiconductor nanoparticles, including future first-principles simulations to be carried out in the project.

(b) Our second simulation paper entitled "High-Throughput Study of Compositions and Optical Properties in Heavily Co-Doped Silicon Nanoparticles" was published in the Journal of Physical Chemistry C and reports the outcome of a detailed study on the effect of dopant distribution within the Si NPs. It is well understood that the donor-acceptor separation between a single donor and acceptor affects the emission energy due to the distance dependent Coulomb attraction between the localized hole and electron. The concentration of boron and phosphorous in heavily co-doped Si NPs can exceed the dopant concentration in bulk Si by multiple orders of magnitude, thus understanding the optical properties in terms of isolated donor-acceptor pairs is not feasible anymore. Prior to our study, the distribution of dopants within the Si NPs, and its role were poorly understood. We investigated 1.6 nm sized Si nanocrystals with fixed, rather high dopant concentration with hundreds of configurations. Utilizing density functional theory and time-dependent density functional theory alongside with Monte-Carlo sampling techniques, we showed that the relative positions of the dopant atoms within the Si NPs have a huge impact on the optical properties. We also found, that the there is a strong correlation between the formation energy of the randomly generated nanocrystals and their optical gaps: the more stable dopant configurations tend to result in higher optical gaps, while less stable configurations could lead to almost metallic nanoparticles. Our results indicate that the optical gaps of co-doped Si NPs can remain quite large even in the case of heavy doping. We created a phenomenological model based on the mean dopant-dopant distances which can be used to approximate the formation energies of co-doped Si NPs before carrying out accurate (but also expensive) DFT calculations. Our model quantifies the effective repulsion between B-B and P-P pairs and the effective attraction between B-P pairs. Overall, our results further the understanding the distribution of dopants within the Si NP as well as the distribution’s significance regarding the optical properties. This could prove to be very useful for our future computational studies of co-doped Si NPs.

(c) We studied the vibrational properties of co-doped Si NPs that was published in the The Journal of Chemical Physics entitled "Photoluminescence, infrared, and Raman spectra of co-doped Si nanoparticles from first principles". This is an important issue as various experimental techniques such as infrared (IR) spectroscopy, Raman spectroscopy and single-dot photoluminescence spectroscopy are among the most important methods that offer insight about the structural properties of co-doped Si NPs. While the vibrational properties of lone donors and acceptors in bulk Si are well understood, this does not hold for heavily co-doped Si NPs. To gain deep understanding about the vibrational properties of co-doped Si NPs, we carried out a systematic study characterizing various few-atomic clusters that are expected to occur in experimental samples. We calculated the vibrational density of states, infrared (IR) absorption spectra, Raman spectra and photoluminescence (PL) spectra for the investigated systems. We found that the energy of the characteristic vibrational signature of substitutional B is strongly dependent on the atoms position within the Si NP. Far from the surface its vibrational energy is the same as in bulk Si, but becomes significantly larger for B atoms in the proximity of the surface. This finding explains the rather broad B-related peak in the Raman spectra of heavily co-doped Si NPs. We concluded that most of the investigated clusters do not exhibit vibrational signatures that can readily be distinguished from each other. The exceptions are clusters involving B-B bonds and three-fold coordinated B atoms at the surface of the Si NP. We also calculated the Raman spectra for a set randomly co-doped Si NPs, where the geometries were taken from our previous publication. We found good agreement with the experimental data, with the exception of a small surface-related high energy peak that is not present in the experimental spectra of larger, co-doped Si NPs. This could imply that the generated electron-hole pair is constrained within the bulk region of the Si NPs. We also calculated the PL spectra for the chosen Si NPs, and compared the results to the experimental single-dot spectroscopy results. Our calculations consistently overestimated the PL energy which can be partly explained by the Quantum Confinement Effect (QCE). On the other hand, the agreement between the simulated vibration-induced broadening and the experimental spectra is very good, both for single NPs and the ensemble. In summary, our study is an important step to pave the way towards the discovery of the correlations between the structural properties of co-doped Si NPs and the measured vibration-related spectra. The result can aid the experimentalists in the interpretation of IR, PL and Raman measurements, and contribute to the structural characterization of co-doped Si NPs.

(d) Our most recent (yet unpublished) results concern the surface properties of heavily co-doped Si NPs. The results of several experimental techniques indicate that the surface of the fabricated co-doped Si NPs is heavily enriched in P and especially B. Recently, it was established by HRTEM measurements that the crystalline core of the co-doped Si NPs is encapsulated by an amorphous shell. The thickness of this shell depends on the B and P concentration of the precursor BPSG film. The presence of this shell is very important as it may explain the co-doped NPs excellent stability against oxidation and aggregation in aqueous solutions. On the other hand, the existence of the amorphous surface layer raises questions about the origin of the PL emission. Amorphous materials exhibit localized states near the conduction and valence band edges, resulting in smaller band gaps compared to their crystalline counterparts. In addition the large concentrations of dopants in the amorphous shell further complicates the picture, with the possible introduction of defects that are unlike the usual donor and acceptor states in bulk semiconductors.

We carried out a systematic study of defects that could possibly occur in the aforementioned amorphous shell. We considered the simplest structural defect: a three-fold coordinated atom. We investigated three-fold coordinated B, P and Si atoms on the surface of a Si NP in different chemical configurations (bonding with different atomic species). This resulted in three families of surface defects related to three-fold coordinated B, P and Si, respectively: B3, P3, Si3.

The family of B3 defects is probably the most interesting. On one hand, three-fold coordinated B atoms could resolve the contradiction that the concentration of B atoms is significantly larger than of P atoms while the electronic structure of the co-doped Si NPs appears to be (almost) perfectly compensated. As boron has only 3 valence electrons, B3 defects are the most natural way to introduce non-active B into Si NPs. On the other hand, three-fold coordinated B introduces a relatively deep unoccupied defect level below the conduction band edge that is localized on the B atom [Fig. 1. a)]. First, we investigated the B3 defect bonding to three Si atoms (B-Si3). We found that the defect becomes shallower with increasing NP size [Fig. 1. a)]. In the light of this result, the nature of the PL emission is possibly also size dependent. For small Si NPs, the excited electron relaxes from the deep, surface-bound defect state by photoemission. For larger Si NPs, the B3 related defect state might be shallower than the bulk donor states of P_{Si}, thus B_3 is irrelevant for the optical properties. Next we studied the various different flavours of the B3 defect by substituting the neighbouring Si atoms by B or P. The results [Fig. 1. b)] indicate that the energy of the resulting defects states changes significantly due to the substitution of its neighbours: substituting the Si atoms with B generally results in shallower defects while P shifts the defect state even deeper in below the conduction band edge.

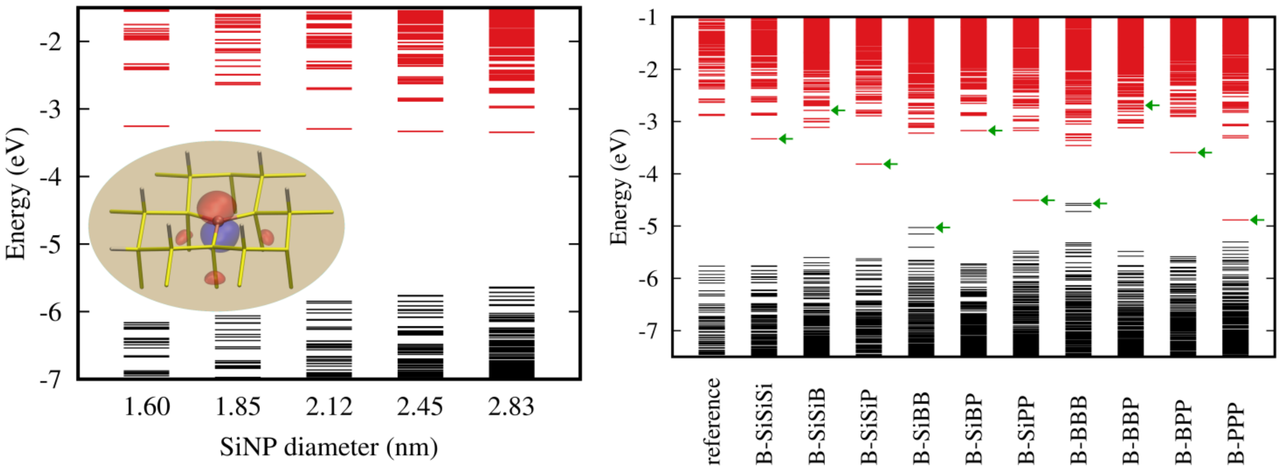

Fig. 1. a) The electronic structure of B-Si3 defect in Si NPs. The inset shows the structure of the defect and the localized defect state. Black and red lines indicate occupied and unoccupied Kohn-Sham levels. b) The electronic structures of various other defects from the B3 family of surface defects. The small green arrows indicate the defect state that is the most localized on the three-fold coordinated B atoms. The reference is the pristine Si NP. Nomenclature: B-XYZ stands for a three-fold coordinated B atoms bonding to an X, Y and Z atom.

The family of P3 defects has the opposite effect on the electronic structure (see Fig. 2.a): they introduce fully occupied defects states above the valence band edge, which are localized on the P atoms as a non-bonding electron pair. Once again, the relative position of the defect state compared to the valence band edge varies depending on the neighbouring atoms.

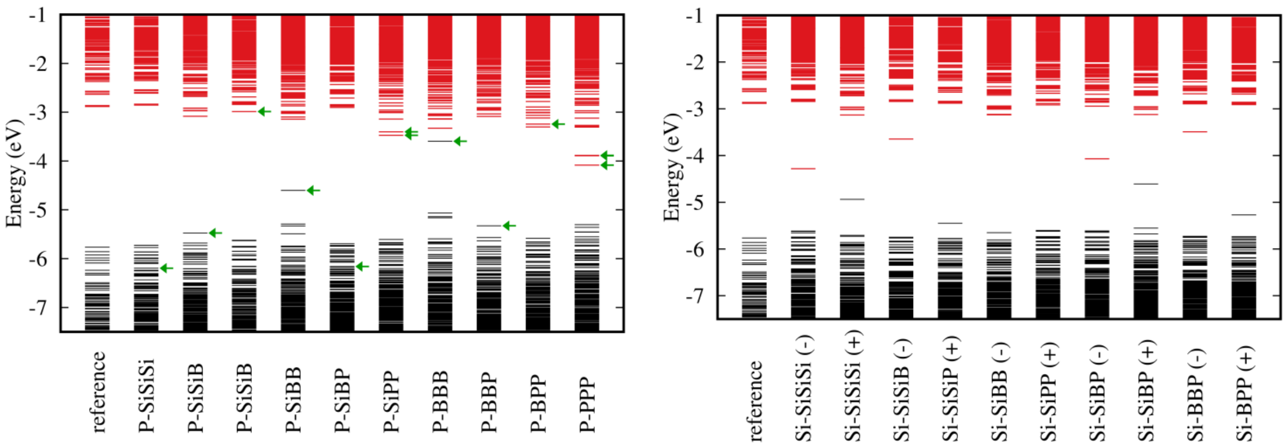

Fig. 2. a) The electronic structure of P3 defects. Black and red lines represent occupied and unoccupied Kohn-Sham states, respectively. The small green arrows indicate the defect states that are the most localized on the three-fold coordinated P atom. b) The electronic structure of Si3 defects. (+) and (-) denote the charge states of the defects.

Finally we investigated the family of Si3 defects. Three-fold coordinated Si atoms introduce dangling bonds with a partially occupied defect state in the gap of the NP. Depending on the chemical potential, this partially occupied state may become fully occupied or empty. The chemical potential depends on the ratio of active B and P dopants as well as the environment of the Si NP. We focused on the negative and positive charge states, leaving the neutral charge state for further investigations. We set the charge states of the Si3 defect by adjusting the number of active B or P dopants in the bulk regions of the Si NP. It is possible that three-fold coordinated Si atoms can contribute to the compensated electronic structure of the Si NPs by absorbing the excess electrons or holes if the concentration of active B and P is not equal. We found that the Si3 family of defects introduces the deepest defect states in the gap (see Fig. 2.b). We identified defects in both negatively and positively charged states that lie in the middle of the gap. These defects most likely become neutral for chemical potentials falling in the middle of the gap.

As a result of our systematic study, multiple defects were identified that can introduce electronic states deep in the band gap of co-doped Si NPs. Our results for the B-Si3 defects indicate that these defects become shallower with increasing NP diameter, but this should be checked for the other defects in the future. These deep defects could possibly play an important role in the optical properties of the co-doped Si NPs, especially for small diameters of NPs. The presence of these defects may also alter the way the optical properties change during the aging of the Si NPs. The conventional bulk-like donor-acceptor states are not significantly influenced by the oxidation of the NP surface. In contrast, the electronic states introduced by the investigated surface defects could be affected by oxidation. For the B3 defects we found that oxidation (formation of a B-O-Si/B/P bridge) shift the unoccupied defect state towards the conduction band edge. If the emission occurs from this defect state, the aging of the NP results in the blue-shift of the PL spectra. For the P3 defects, we found a similar trend, although to a much lesser magnitude. We note that the P-O bond is much weaker than the Si-O and B-O bonds, thus the formation of P-O-Si/B/P bridges is very unlikely. This fact might explain the oxidation resistance of heavily co-doped Si NPs. The oxidation of the Si3 structures influences the depth of the defect state in a more intricate manner: for positively charged defects, the defect state becomes shallower due to oxidation. For negatively charged Si3, the effect of oxidation is the opposite. In both cases however, the overall effect of oxidation is rather small.

Finally, we discuss the prevalence of the investigated defects. This is a rather difficult task, as the computational cost of molecular-dynamics studies is prohibitively expensive. As a consequence, comparing the formation energies of the defects is the best approach to estimate the likelihood of their presence in experimental samples. The determination of formation energies is also non-trivial, as it requires knowledge about the formation of the given defect. In this highly complex case, where the formation of co-doped Si NPs from the annealed boron-phosphorus-silicon-glass matrix is not well understood, we have to make some compromises. We compare the formation energies of the various investigated defects, we compare the energies of the B-XYZ defects to a B-Si3 defect, and account for the Si→X/Y/Z substitution by using the formation energies of isolated B/P atoms. For the B3 family of defects, our results indicate that most of the investigated defects cannot be ruled out by energetical considerations. B-PPP and B-BBB defects seem to be the least energetically stable, while B-SiSiP, B-SiBP, B-BBP and B-BPP all have low formations energies. In case of the P3 family of defects, most of the studied defects are less stable compared to P-Si3, indicating that this family of defects is not likely to introduce deep defect levels. For the Si3 defects, we find that the structures that introduce deeper defect states in the gap are energetically less favoured than the structures that introduce shallower defect states.

ii) Silicon carbide nanoparticles

Jan Valenta, the coordinator of the consortium, and Marie Kalbačova proposed to initiate experiments on SiC NPs that are prepared and developed at Wigner ADMIL by our research group. We prepared and shipped SiC NPs with 1-3 nm and 4-6 nm of diameter to Valenta's group, Kalbačova's group and Anna Furnikova for further examinations. The properties of individual SiC NPs, the toxicity of different surface termination as well as size separation possibilities have been tested. We also sent samples to Robert Mroczyński to the Warsaw University of Technology for potential application of SiC NPs in metal–insulator–semiconductor (MIS) structures. Most of these joint experimental studies need further efforts, however, we already presented some results from these collaborations in a physical chemistry journal (see below). The other results were published in three scientific journals. The main thesis points of these studies are listed below.

(a) Our paper entitled "Harnessing no-photon exciton generation chemistry to engineer semiconductor nanostructures" was published in Nature Publishing Group Scientific Reports, and it reports the fabrication, shape and size control of silicon carbide nanoparticles. We demonstrated that, by engineering hexagonal inclusions into the cubic silicon carbide, selective etching can be achieved. The underlying mechanism was identified as a no-photon exciton generation chemistry (NPEGEC) process, enabled by the substantial energy difference between the conduction band minima of the cubic and hexagonal polytypes of silicon carbide. The selective etching method demonstrated in this work can potentially utilized for other polytypic compound semiconductors, providing a valuable tool for the fabrication of semiconductor nanostructures with intricate patterns.

(b) Our paper entitled "Surface-Mediated Energy Transfer and Subsequent Photocatalytic Behavior in Silicon Carbide Colloid Solutions" was published in Langmuir and demonstrates the effect of particle-particle interaction of colloids on the photocatalytic efficiency. We found that SiC NPs of sizes between 4 and 10 nm show photocatalytic activity, while smaller 1-4 nm sized SiC NPs do not. We identified that the both the size distribution and the surface chemistry of the SiC NPs affect the overall photocatalytic efficiency of the system, as carboxyl-terminated SiC NPs form temporary type I-like junctions while hydroxyl-terminated particles do not assemble. These findings have implications for the potential biological and photocatalytic applications of SiC NPs.

(c) We studied the size engineered SiC NPs further in collaboration with Jan Valenta and Anna Furnikova. We used single particle spectroscopy developed by Jan Valenta and precise AFM measurements to describe the size and surface dependence of the optical properties of SiC NPs. We reported our results in the Journal of Physical Chemistry C, entitled "Direct Observation of Transition from Solid-State to Molecular-Like Optical Properties in Ultrasmall Silicon Carbide Nanoparticles". In this joint study, we showed the transformation of optical properties from semiconductor to molecular nature.

(d) Our paper entitled "Identification of the binding site between bovine serum albumin and ultrasmall SiC fluorescent biomarkers" in the Journal of Physical Chemistry C describes the size dependent interaction of NPs and the BSA proteins, where BSA proteins simulate the environment of human blood. We used advanced spectroscopic methods to understand how NPs and proteins interact when the size of the nanoparticles is much smaller than the size of the proteins. We showed by combined advanced optical measurements and theoretical studies that, in the absence of usual secondary interactions, a temporary physical complex is formed, when ultrasmall NPs are engulfed by proteins because of the presence of pockets and binding sites.

The list of published papers with complete references is given in the report of publications.

Involvement of student and youth researchers

In the *ab initio* simulation thrust, one youth researcher (Bálint Somogyi) received a PhD degree. Another youth researcher (Viktor Ivády) worked on the implementation of the calculation of spin-related properties that will be applied in the surface study of Si NPs. Emilie Bruyer worked relatively short time in the project and contributed to the calculation of the infrared vibration spectrum. In the preparation and analysis of SiC NPs thrust, one youth researcher (Dávid Beke) received a PhD degree. Another youth researcher (Gyula Károlyházy) has become a PhD candidate. These two young researchers could supervise chemical engineer students from the Budapest University of Technology and Economics in this project (Klaudia Horváth, Boglárka Móricz, Dániel Unyi, Fanni Oláh, Dávid Veres, Dániel Áron Major, Mátyás Mihály Rudolf, Balázs Juhász). Two of them were graduated at BSc level whereas four of them were graduated at MSc level, and the MSc graduation for two of them (Mátyás Mihály Rudolf and Balázs Juhász) is in progress. The complete list of graduated and postgraduate students can be found below:

PhD

Bálint Somogyi (2017), “First principles study of silicon carbide nanocrystals”

Dávid Beke (2017), “Fabrication and characterization of silicon carbide nanoclusters”

MSc

Fanni Oláh (2019), “Szilícium-karbid előállítása és anyagszerkezeti vizsgálata”

Dávid Veres (2019), “SiC nanorészecskék felületének összehasonlító elemzése”

Dániel Áron Major (2019), “Marhaszérum-albumin fehérje szilícium-karbid nanoklasztereivel való kölcsönhatásának és fluoreszcenciás feljelölésének vizsgálata”

Boglárka Móricz (2017), “Szilícium-karbid nanokristályok méretszeparálása”

BSc

Dániel Unyi (2017), “Hidroxilált szilícium-karbid nanokristályok szintézismódszerének fejlesztése”

Klaudia Horváth (2016), “Szilícium-karbid nanokristályok fotokémiai tulajdonságainak vizsgálata”

Dissemination

The results were presented at international conferences and workshops. The results were well accepted as three oral presentations were invited talks. The third invited talk is, in particular, highlighted, which was presented in a highly prestigious conference about Si related materials. The members of the consortium and Milos Nesladek organized a symposium about semiconductor nanostructures at the Fall Meeting of the European Materials Research Society in 2018. One popular talk was also given in 2018. The list of presentations is given below.

Conferences:

1. Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals, E-MRS Spring Meeting and Exhibit, Lille (France), May 2-6, 2016 **(Dávid Beke, Graduate Student Award)**
2. **Invited talk:** Design and characterization of nanostructures: theory and experiment hand in hand, European Materials Research Society Fall Meeting, Warsaw (Poland), September 18-22, 2016 (Ádám Gali)
3. Investigation of heavily co-doped Si NPs by first principles simulations, E-MRS Fall Meeting, Warsaw (Poland), September 18 - 21, 2017 (Bálint Somogyi)
4. Size dependent photocatalytic activity of silicon carbide nanoparticles, E-MRS17 Fall Meeting Warsaw, Poland, September 18-20, 2017 (Dávid Beke)
5. Controlling the size of cubic silicon carbide nanoparticles by engineering the hexagonal inclusion, E-MRS17 Fall Meeting, Warsaw, Poland, Sept. 18-20, 2017 (Dávid Beke)
6. Size Selective Optical and Photocatalytical Properties of Silicon Carbide Nanoparticles, NanoMat17, Budapest, Hungary, September 24-27, 2017 (Dávid Beke)
7. **Invited talk:** Size Selective Optical and Photocatalytical Properties of Silicon Carbide Nanoparticles, CMSE 2018, Xi'an, China, November 1-4, 2018, (Dávid Beke)
8. No-photon exciton generation chemistry for size selective synthesis of ultrasmall silicon carbide nanoparticles, E-MRS18 Spring Meeting, Strasburg, France, June 18-22, 2018 (Dávid Beke)
9. **Invited talk:** Ab initio theory on heavily co-doped silicon nanocrystals, 9th European Symposium on Silicon, Saarbrücken (Germany), September 9-12, 2018 (Ádám Gali)
10. Identification of the vibrational signals of B and P co-doped Si nanocrystals by first principles simulations, Workshop on Silicon Nanoparticles, Bertinoro (Italy), October 1-3, 2018 (Bálint Somogyi)

Popular talks:

David Beke: Researchers‘ night – Sep. 28-29, 2018. “The unusual properties of nanoparticles.”

Organization of conferences:

Symposium T: Silicon, germanium, diamond and carbon nanostructures and their nanocomposites with other materials, in the framework of E-MRS Fall Meeting, September 18-20, 2017, Warsaw. Organizers: J. Valenta, M. Fujii, A. Gali and M. Nesladek. Selected papers published in physica status solidi, organizer were “guest editors“. There were 56 contributions (35 oral, 21 posters).

Summary and outcome

Our studies were published in seven prestigious journals, including a Nature Publishing Group journal, about silicon and silicon carbide nanoparticles. The major outcome of this research consortium is, on the other hand, the creation of new cooperation between research groups that had been not worked together. In particular, the cooperation between the Czech groups and Ádám Gali group has become very useful in the experimental thrust in which Dávid Beke from Ádám Gali group stayed two weeks to learn new preparation and optical methods at Charles University in Prague. The cooperation continues with the measurements of single SiC nanoparticles that are prepared in Ádám Gali group. At the theoretical thrust, novel cooperation between the Slovakian group and Ádám Gali group has been developed in which the DFT methods can be assessed by advanced QMC methods. Furthermore, the experimental Japanese group continues to cooperate with Ádám Gali in the investigation of Si and other semiconductor nanoparticles. Young researchers and students joint to this research resulted in two PhD degrees and diploma works, and further graduation is expected in the near future. The joint efforts can lead to the development of *in vivo* bioimaging agents and absorbers for third generation solar cells.

Budapest, February 24, 2019

Dr. Ádám Gali
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