

Workshop on

Advancement of Group IV Nanostructures Nanophotonics and Nanoelectronics

November 18-19, 2014

Takikawa Memorial Hall, Kobe University,

Rokkodai, Nada, Kobe 657-8501, Japan

(<http://www.kobe-u.ac.jp/en/access/rokko/campus.html>)

Organization:

1. Japan-Czech bilateral joint research project (JSPS) 
2. Smart materials team in organization of advanced science and technology, Kobe University.



Program

Tuesday, November 18

13:30 Welcome address

[Electronic and photonic applications I \(Chair: Minoru Fujii\)](#)

13:35 Shunri Oda, *Quantum Nanoelectronics Research Center, Tokyo Institute of Technology*

Si quantum dots for future electronics and photonics

14:10 Tom Gregorkiewicz, *Van der Waals – Zeeman Institute, University of Amsterdam*

Si nanocrystals in SiO₂ for spectral shaping in future photovoltaics

14:45 Stefano Ossicini, *Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia*

Silicon nanostructures for photonics and photovoltaic applications

15:20-15:40 Break

15:40 Nobuyoshi Koshida, *Graduate School of Engineering, Tokyo University of Agri. & Tech.*

Diverse functional applications of nanostructured silicon

[Material Synthesis \(Chair: Xiaodong Pi\)](#)

16:15 Naoto Shirahata, *National Institute for Materials Science (NIMS)*

Organically-Terminated Silicon Nanoparticles: Synthesis, Separation by Emission and Applications

16:50 Anna Fucikova, *Department of Chemical Physics and Optics, Charles University in Prague*

Various ways of preparing and modifying silicon nanocrystals

17:25 Vladimir Svrcek, *National Institute of Advanced Industrial Science and Technology*

Surface and energy band gap engineering of silicon nanocrystals

18:15-20:00 Banquet (Ground floor)

Wednesday, November 19

Photonics and characterization technique (Chair: Tom Gregorkiewicz)

9:00 Bernard Gelloz, *Graduate School of Engineering, Nagoya University*

Characteristics of nano-porous silicon luminescence and electroluminescence, and effects of various treatments

9:35 Kenji Imakita, *Graduate School of Engineering, Kobe University*

CMOS-compatible nonlinear optical materials for Si photonics

10:10-10:30 Break

10:30 Jan Valenta, *Faculty of Mathematics & Physics, Charles University*

Special techniques of optical spectroscopy applied to Si nanostructures

11:05 Masashi Ishii, *National Institute for Materials Science (NIMS)*

Charge transfer dynamics of "Bright" and "Dark" Si-nc's

Electronic and photonic applications II (Chair: Tom Gregorkiewicz)

11:40 Tomohiro Nozaki, *Department of Mechanical Sciences and Engineering, Tokyo Institute of Technology*

Silicon nanocrystals and hybrid solar cells

12:15-13:30 Lunch

Doping (Chair: Stefano Ossicini)

13:30 Minoru Fuji, *Graduate School of Engineering, Kobe University*

All-Inorganic Colloidal Silicon Nanocrystals

14:05 Xiaodong Pi, *State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University*

Localized surface plasmon resonance of B- and P-doped Si nanocrystals

14:40 Naoki Fukata, *National Institute for Materials Science (NIMS)*

Doping and characterization of impurity atoms in Si and Ge nanowires

Biological applications (Chair: Minoru Fujii)

15:15 Antonin Broz, *Faculty of Medicine, Charles University*

Challenges in work with nano-crystals in cell biology

15:50 Closing remark

16:00- Lab. tour (Mesoscopic materials laboratory, Kobe University)

Language: English

Participation is open to whole academic community and it is free of charge.

Organizers: Minoru FUJII, Kenji IMAKITA, Kanna AOKI, Shinya KANO

Department of Electrical and Electronic Engineering, Graduate School of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, JAPAN

fujii@eedept.kobe-u.ac.jp, Tel: +81-(0)78-803-6081

Abstracts

Si quantum dots for future electronics and photonics

Shunri Oda

Quantum Nanoelectronics Research Center, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku,

Quantum dot structures, where electrons are confined three-dimensionally in the sub-10 nm scale, show characteristics quite different from conventional bulk structures. Recent progress in the fabrication technology of silicon nanostructures has made possible observations of novel electrical and optical properties of silicon quantum dots, such as single electron tunneling, ballistic transport, visible photo-luminescence and high-efficiency electron emission.

Silicon quantum dots are fabricated either by bottom-up or top-down processes. Fabrication and electrical/opto-electrical characterization of nanocrystalline Si films by plasma processes and coupled Si quantum dots by electron beam lithography processes are discussed.

Si nanocrystals in SiO₂ for spectral shaping in future photovoltaics

T. Gregorkiewicz

Van der Waals – Zeeman Institute, University of Amsterdam
Science Park 904, 1098 XH Amsterdam, The Netherlands

The most important limitation for efficiency of photovoltaic energy conversion appears due to the mismatch between the broad-band character of the solar radiation and the discrete operation mode of solar devices, as determined by the specific bandgap energy of the active medium. One remedy for that would be the spectral transformation of the solar radiation before it enters a photovoltaic device. Specifically, such a “solar shaper” should split the large energy photons into smaller ones, whose conversion efficiency is optimal.

In my presentation, I will discuss how shaping of the solar spectrum can be achieved using layers of Si nanocrystals with and without Er doping. In such systems efficient photon transformation can be realized by quantum cutting [1] and/or emission from Er³⁺ ions sensitized by Si nanocrystals [2]. I will present evaluation of external quantum efficiency of emission from thin layers of Si nanocrystals in SiO₂ and its evolution upon introduction of Er³⁺ ions. Using differently prepared materials I will evaluate how this can be maximized. I will also discuss energy efficiency of solar shapers based on Si nanocrystals and Er³⁺ ions. In a separate part, I will discuss also strategies how Si nanocrystals can be employed for quantum “pasting” by which low-energy photons could be used in photovoltaic conversion by a standard Si solar cell.

[1] M.T. Trinh *et al.*, Nature Photonics 6, 316-321 (2012).

[2] S. Saeed *et al.*, Nature Communications 5:4665 (2014)

Silicon nanostructures for photonics and photovoltaic applications

Stefano Ossicini

CNR-INFM-S³ “nanoStructures and bioSystems at Surfaces”, Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia, via Amendola 2 Pad. Morselli, I-42100 Reggio Emilia, Italy

stefano.ossicini@unimore.it

In recent years particular attention has been devoted to Silicon nanocrystals and nanowires, a powerful class of nanostructures which is opening new substantial opportunities for photonics and photovoltaics. These nanostructures are zero- and one-dimensional materials with diameter from few to some tenths of nanometers. They present unique size dependent electronic, optical and transport properties that are intrinsically associated with their low dimensionality and quantum confinement effect (QCE). In particular we have performed several ab-initio calculations in the framework of Density Functional Theory and Many-Body Perturbation Theory for free and silica embedded Si nanocrystals and for Si and Si-Ge nanowires. Among the different results we will concentrate, here, on Si nanocrystals and on SiGe nanowires.

In this latter case we show that efficient *n*- and *p*-type doping can be achieved in coaxial SiGe nanowires, taking advantage of the band offset of the Si/Ge interface. A one-dimensional electron (hole) gas is created at the band-edge and the carrier density is uniquely controlled by the impurity concentration with no need of thermal activation. Additionally, SiGe core-shell nanowires provide naturally the separation between the different types of carriers, electron and holes, a property ideally suited for photovoltaic applications.

In the first case, the opportunity of doping and codoping of Si nanocrystals embedded in a SiO₂ matrix or passivated by H or OH groups has been considered in order to tune their transport and/or optical properties. Moreover we will show how the interaction between nanocrystals is a promising route to foster the establishment of third generation photovoltaics due to multiple exciton generation.

Diverse Functional Applications of Nanostructured Silicon

Nobuyoshi Koshida

Graduate School of Engineering, Tokyo University of Agri. & Tech.,
Koganei, Tokyo 184-8588, Japan,
e-mail: koshida@cc.tuat.ac.jp
URL: <http://www.tuat.ac.jp/~koslab/>

Along with the continuing development of ULSI for large-capacity and lower-power information processing, silicon technology has been explored toward functional applications in photonics, acoustics, MEMS, sensing, biometric, and biomedical area. Here we show that nanostructured silicon is a platform for the emerging diverse streams. A typical fabrication method of nanosilicon is a wet process termed electrochemical anodization. Depending on the anodization conditions and the type of silicon substrates, two kinds of structures are formed in the etched layers: interconnected nanodots and periodically arrayed nanopores. Prepared quantum-sized silicon dots which behave as a quasi-direct wide-gap semiconductor provide opportunities for silicon photonics: efficient light emitter in visible to uv range and photovoltaic conversion in the short wavelength region. Analyses of observed avalanche photoconduction indicate that the impact ionization rate in nanosilicon dots is considerably higher than that in bulk silicon. The hot electron effect leads to the development of ballistic cold cathode. The usefulness as an energetic planar electron emitter has been demonstrated in vacuum (parallel EB lithography), in atmospheric-pressure gases (electron attachment), and in solutions (ballistic electro-deposition of thin metal and group-IV films). The extremely lowered thermal conductivity of nanosilicon induces efficient thermo-acoustic effect with a broad-band response. This is useful as a full-digital speaker and an analytical tool of bio-acoustic communications. The nanosilicon layer with high aspect-ratio periodic nanopores is useful as a template for fabricating Ni nanowire arrays with a significantly high magnetic anisotropy. Some topics on these functional properties of nanosilicon are discussed, including their device applications.

Organically-Terminated Silicon Nanoparticles: Synthesis, Separation by Emission and Applications

Naoto Shirahata^{1,2}

¹WPI-MANA, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba 305-0047, ²PRESTO, Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, 332-0012, Japan E-mail: shirahata.naoto@nims.go.jp

Optical use of colloidal nanoparticles of silicon (npSi) and germanium (npGe) has gained increasing attention for its possible contributions to building a sustainable society that ideally uses resources and energy with high efficiency without causing damage to the environment or human health. Full control in nanostructures such as crystalline phase, surface and size of the NPs allows the tuning the color in a very broad range of emission wavelength from near-UV (300 nm~) through full color of visible to near-IR (~1030 nm for npSi and ~1270 nm for npGe). However, the story does not end here. Unlike the direct bandgap semiconductors, PL origin of npSi is still not very clear and under debate. The yet-to-be-defined mechanism becomes a big obstacle for ease in access to emission tuning. As a result, research on luminescent Si is a matter for fundamental study. A lot of reports regarding the emission is very interesting counter-intuitive and even confusing and to reach in a unified conclusion. From the reported literatures emission of npSi can be divided into two distinct regions. First region is in the emission range from near-UV to Aqua (λ_{em} = 300–500 nm), and another region is Green to NIR (λ_{em} = 500–1030 nm) region. There is a discontinuity or wall between these two regions. These two kind of different emission zone, covered by npSi are being prepared by fundamentally different preparation approaches. To the best of our knowledge, unfortunately, there are no reports which break this barrier or discontinuity smoothly by a single preparation method. In the present talk, I will start my talk by describing the synthesis of npSi with diamond cubic lattice structures. A critical size of npSi to form a diamond cubic lattice lies in the range between 1.1 and 1.2 nm. Thus, we can see the size dependent photoluminescence spectra in the range between 500 nm and 1130 nm through the control over the size of diamond cubic npSi in the ranging from 1.1-1.2 nm to 5.2 nm. On the other hand, we see the size-dependent NUV-Aqua emissions when npSi do not have diamond cubic lattices. Commonly, the NUV-Aqua emitting npSi are prepared by any solution synthesis under room temperature and subsequent column separation by emission color. The discovery of color-tunable emission from free-standing npSi kindled the development and study of luminescent forms of Si for its potential applications. I will show herein several applications including light-emitting diodes.

1. For reviews, see: a) B. Ghosh and N. Shirahata, "Solution-Processable White-Light-Emitting Germanium Nanocrystals", *Sci. Technol. Adv. Mater.* 2014, 15, 014207 (1-14) b) N. Shirahata, "Colloidal Si nanocrystals: A controlled organic-inorganic interface and its implications of color-tuning and chemical design toward sophisticated architectures", *Phys. Chem. Chem. Phys.* 2011, 13, 7284-7294. c) N. Shirahata, A. Hozumi, T. Yonezawa, "Monolayer-derivative Functionalization of Non-oxidized Silicon Surfaces", *Chem. Rec.* 2005, 5, 145-159
2. B. Ghosh, Y. Masuda, Y. Wakayama, Y. Imanaka, J. Inoue, K. Hashi, Deguchi, H. Yamada, Y. Sakka, S. Ohki, T. Shimizu, and N. Shirahata, "Hybrid White Light Emitting Diode Based on Silicon Nanocrystals", *Adv. Funct. Mater.* 2014 (DOI: 10.1002/adfm.201401795)
3. N. Shirahata, D. Hirakawa, Y. Masuda, and Y. Sakka, "Size-Dependent Color-Tuning of Efficiently Luminescent Germanium Nanoparticles", *Langmuir* 2013, 29, 7401-7410
4. N. Shirahata, "Solution-Processable White-Light-Emitting Germanium Nanocrystals" *J. Sol. Stat. Chem.* 2014, 214, 74-78
5. B. Ghosh, Y. Sakka, and N. Shirahata, "Efficiently Green-Luminescent Germanium Nanocrystals", *J. Mater. Chem. A* 2013, 1, 3747-3751
6. N. Shirahata, D. Hirakawa, and Y. Sakka, "Interfacial-related Color Tuning of Colloidal Si Nanocrystals", *Green Chem.* 2010, 12, 2139-2141
7. N. Shirahata and Y. Sakka, "Controlled Organic/Inorganic Interface Leading to the Size-tunable Luminescence from Si Nanoparticles", *J. Cer. Soc. Jpn.* 2010, 118, 932-939
8. N. Shirahata, T. Tsuruoka, T. Hasegawa, and Y. Sakka, "Size-Tunable UV-Luminescent Silicon Nanocrystals", *Small* 2010, 6, 915-921
9. N. Shirahata, M. R. Linford, S. Furumi, L. Pei, Y. Sakka, R. J. Gates, M. C. Asplund, "Laser-derived One-Pot Synthesis of Silicon Nanocrystals Terminated with Organic Monolayers", *Chem. Commun.* 2009, 4684-4686

Title: Various ways of preparing and modifying silicon nanocrystals

Anna Fucikova, *Department of Chemical Physics and Optics, Charles University in Prague
Czech Republic*

Contact: *anna.fucikova@email.cz*

In this presentation we would like to summarize various methods of silicon nanocrystals preparation and present the pros and cons of each method. Especially we concentrate on preparation of nanocrystals from hydrogen silsesquioxane (HSQ). The silicon nanocrystals are formed from HSQ molecules annealed at 1000°C in inert Ar atmosphere with 5% H₂. In this way, we obtain silicon nanocrystals in silicon oxide matrix. The nanocrystals are released from the matrix by HF etching and need to be stabilized in order to prevent the nanocrystals from deterioration. In the stabilization process the surface Si-H group is usually replaced by an organic group. This process can be initiated by light, high temperature, microwaves, or radicals. The properties of passivated nanocrystals are varying greatly in quantum efficiency, PL peak position and width.

In cooperation with J. Linnros group we also developed a method for direct passivation of silicon nanocrystals in the annealing step. The individual silicon nanocrystals exhibited significantly narrow emission peak at room temperature (average linewidth ~ 25 meV) compared to silicon nanocrystals embedded in a silicon oxide shell (150 meV), when studied by single dot spectroscopy. The luminescence from produced nanocrystals covers a broad spectral range from 530-720 nm (1.7-2.3 eV). Blinking and spectral hopping of individual nanocrystals were also detected. The silicon nanocrystals did not show any deterioration of luminescence for at least 16 months.

Surface and energy band gap engineering of silicon nanocrystals

Vladimir Svrcek¹, Mickael Lozach¹, Somak Mitra² Davide Mariotti²,

¹ National Institute of Advanced Industrial Science and Technology, Research Center for Photovoltaic Technologies, Tsukuba, Japan.

² University of Ulster, Nanotechnology & Integrated Bio-Engineering Centre-NIBEC, Newtownabbey, UK.

In 1st/2nd generation devices, every absorbed photon can only generate one electron-hole pair whereby in devices with carrier multiplication (CM), more than one electron-hole pair can be formed for every photon absorbed. CM has been demonstrated to occur in PbSe, PbS, PbTe, CdSe, InAs and Si quantum dots (Si QDs) [1]. In this context, silicon as a raw material represents an attractive solution; however CM in Si QDs is triggered only for high energy photons (above ~2 eV) [2] and the indirect nature of silicon still plays a role in limiting the absorption coefficient.

In this talk we discuss how surface engineering and alloying bulk Si with another material offers another opportunity to challenge the nature of silicon's indirect energy band gap in Si QDs. In this respect the atmospheric generated plasmas present unique opportunities. In particular atmospheric pressure confined plasma (e.g. microplasmas) has allowed substantial promising advances for both QDs surface engineering and synthesis. Firstly, here we would like to report on recent strategies for surfactant free surface engineering of Si QDs that have employed microplasma interactions with colloids [3]. The surface characteristics achieved via microplasma processing contributed to improve optoelectronic properties, add to our understanding of Si QDs fundamental properties [4-6] and made possible the fabrication of photovoltaic devices with improved efficiencies [7]. Secondly we discuss the approaches how to engineer the energy band gap and direct transition in Si QDs by alloying with environmental friendly and abundant element (e.g. tin). Confined plasmas generated in the liquid by ns/fs laser pulses allowed the growth of the silicon-tin QDs via kinetic pathways. In particular we would like to report on the synthetic feasibility of semiconducting alloyed silicon-tin QDs where the silicon-tin alloys at quantum confinement size have the potential to undergo a real transition from indirect to direct narrower energy bandgap, compared to corresponding elemental Si QDs [8].

Acknowledgements This work was partially supported by a NEDO and JSPS projects, international network through the Leverhulme Trust Grant.

References

1. P. V. Kamat *J. Phys. Chem. Lett.* **2013**, 4, 908
2. D. Timmerman et al. *Nat. Nanotechnol.* **2011**, 6, 710L18
3. V. Svrcek et al. *Applied Physics Letters* **2010**, 97, 161502
4. D. Mariotti, et al *Adv. Funct. Mat.* **2012** ,22, 954.
5. V. Svrcek et al. *J. Phys. Chem. C* **2013**, 117, 10939
6. V. Svrcek et al. *Adv. Funct. Mater.* **2013**, 23, 6051
7. V. Svrcek et al. *Appl.Phys.Lett.* **2012** , 100, 223904
8. V. Svrcek et al. *Nanoscale*, **2013**, 5, 6725

Characteristics of nano-porous silicon luminescence and electroluminescence, and effects of various treatments.

Gelloz Bernard

Nano porous silicon can be prepared by electrochemical etching of silicon wafers in hydrofluoric acid. Luminescent layers can be obtained when the porous structure contains crystallites whose sizes are lower than the Bohr radius in silicon (~4 nm).

Regarding optoelectronic applications, compared to other nano-silicon materials obtained by planar technologies, porous silicon has a set of key advantages, such as (i) the ease and low-cost of manufacture, (ii) the ability to form quickly thick layers (limited only for the silicon substrate thickness), and (iii) easy modulation of index for photonic crystal formation. However, it also has critical limitations, such as (i) mechanical weakness of high porosity layers, (ii) an easily contaminated exposed surface (it is an opened structure) leading to poor stability, and (iii) a difficult control of feature size distribution within the porous silicon skeleton.

This presentation reviews the luminescence and electroluminescence properties of porous silicon. In addition, various treatments used in a view to enhancing their characteristics (such as efficiency, stability, color) are reviewed.

CMOS-compatible nonlinear optical materials for Si photonics

Kenji Imakita

Graduate School of Engineering, Kobe University

In recent years, nonlinear optical phenomena in Si-based materials have attracted significant attentions due to the possible optoelectronic applications such as all optical signal routing, wavelength converter, electro-optic modulator, and so on. It is well known that Si crystal shows small third order nonlinearity compared to direct bandgap semiconductors due to the indirect bandgap nature, and exhibits no second order nonlinearity due to the centrosymmetric structure. These motivate researchers to explore new CMOS-compatible materials with large second or third order nonlinearity.

This work consists of two parts. The first part is on the third order nonlinear optical properties of phosphorous(P)- or boron(B)-doped silicon nanocrystals embedded in SiO₂ thin films prepared by a sputtering method. A z-scan method and a pump-probe optical kerr gate method were used to evaluate the nonlinear refractive index (n_2), two photon absorption coefficient (β), and the time response of the third order optical nonlinearity. The values of n_2 and β of our undoped samples were the order of 10^{-12} cm²/W and 10^{-9} cm/W, respectively. Regardless of P- or B-doping, n_2 and β were found to be enhanced about 5 times by the doping. The time response of the optical nonlinearity was faster than our time resolution of 100 femtoseconds. The results indicate that doping of Si nanocrystals can be a promising tool to improve the nonlinear optical properties.

The second part is on the second order nonlinearity of CMOS-compatible amorphous thin films. Until recently, it was believed that amorphous materials do not show second order nonlinearity due to the centrosymmetric structure. However, a few kinds of amorphous thin films prepared by conventional deposition systems, such as SiN thin films prepared by plasma enhanced chemical vapor deposition and silicon monoxide (SiO) thin films prepared by an electron beam deposition, have been reported to exhibit large second order nonlinearity. In this work, we investigated the second order nonlinearity of Ge-doped SiO₂ amorphous thin films prepared by a sputtering method. It was found that the second-order nonlinearity of SiO₂, which vanishes in the electric-dipole approximation, can be significantly enhanced by Ge doping. The observed maximum value of d_{33} is 8.2 pm/V, which is 4 times larger than d_{22} of β -BaB₂O₄ crystal. Strong correlation was observed between the d_{eff} values and the electron spin resonance signals arising from GePb centers, suggesting that GePb centers are the most probable origin of the large second-order nonlinearity.

Special techniques of optical spectroscopy applied to Si nanostructures

Jan Valenta

*Department of Chemical Physics & Optics, Faculty of Mathematics & Physics, Charles University,
Prague 2, Czechia*

jan.valenta@mff.cuni.cz

Light-emitting silicon nanostructures have been studied for more than 25 years, but the full understanding of electronic and optical properties is still not achieved. We believe that application of advanced techniques of optical spectroscopy can move forward our knowledge of Si nanostructures. Namely the following techniques have great potential: single-nano-object spectroscopy, non-linear optical spectroscopy, quantum yield measurement etc. All these techniques require careful calibration and reliable sample preparation, otherwise severe artefacts could distort the obtained results. In this contribution we shall discuss some critical aspects of these spectroscopy techniques.

Charge transfer dynamics of “Bright” and “Dark” Si-nc’s

Masashi Ishii

National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan

ISHII.Masashi@nims.go.jp

“Bright” Si-nc’s can be investigated with optical measurements such as photoluminescence. However, how can we investigate “Dark” Si-nc’s? From the fact that charge transfer decides “Bright” or “Dark” of Si-nc’s, we adopt electronic measurement techniques for complete understanding of nano-systems including “Bright” and “Dark” Si-nc’s.

To discuss dynamics of the charge transfer, we performed electronic frequency response analyses (FRA). By using the FRA, we can precisely probe specific charge behaviors with response time τ from \sim ps to \sim s. We found that Si-nc systems have charge responses in μ s \sim ms region [1-3]: The faster electron-hole recombination process with $\tau \sim \mu$ s is a reason of intense emission of Si-nc’s, the activation process of a dopant level with $\tau \sim$ ms fills the Si-nc’s with charges, and Auger recombination with $\tau \sim 100$ ms emits the filled charges and quenches the luminescence.

I talk various charge behaviors in photo-excited Si-nc’s and approach the factors determining “Bright” and “Dark” of the Si-nc’s.

This work was supported by KAKENHI, Grand-in-Aid for Scientific Research (26420287).

- [1] M. Ishii, I. Crowe, M. Halsall, A. Knights, R. Gwilliam, and B. Hamilton, *J. Appl. Phys.* **116**, 063513 (2014).
- [2] M. Ishii, I. Crowe, M. Halsall, A. Knights, R. Gwilliam, and B. Hamilton, *Jpn. J. Appl. Phys.* **53**, 031302 (2014).
- [3] M. Ishii, I. Crowe, M. Halsall, A. Knights, R. Gwilliam, and B. Hamilton, *Appl. Phys. Lett.* **101**, 242108 (2012).

Silicon nanocrystals and hybrid solar cells.

Tomohiro Nozaki and Yi Ding

Department of Mechanical Sciences and Engineering, Tokyo Institute of Technology

tnozaki@mech.titech.ac.jp

This paper presents synthesis method of highly crystalline silicon nanocrystals (Si NCs) and application to organic/inorganic hybrid solar cell. Si NCs with mean size of 6 nm were synthesized from chlorinated silicon precursor (SiCl_4) using flow-type, non-thermal VHF (70 MHz) plasma reactor. Si NCs, as an electron acceptor, were blended with p-type organic semiconductor materials (P3HT or PTB7) using appropriate solvent, producing stable Si NCs containing inks. After spin casting on ITO substrate and evaporation of metal contact, it forms bulk heterojunction (BHJ) type organic/inorganic hybrid solar cells with isolated Si NCs in the polymer matrix. Performance was evaluated under 1-SUN (100 mW/cm^2), resulting in short circuit current of 11.5 mA/cm^2 , open circuit voltage of 0.62 V, and power conversion efficiency of 3.7%. The electronic band structure and its tunability by size and surface termination; -Cl (as produced), -H (HF treatment), -O (controlled oxidation) is the key to maximizing the power conversion capability of the device. Examining the performance of those devices would offer valuable insights into the electronic band structure of Si NCs and their tunability. Successful fabrication of highly efficient and inexpensive solar cell with Si NCs is the important goal to meet the future energy demand.

All-Inorganic Colloidal Silicon Nanocrystals

Minoru Fujii

Department of Electrical and Electronic Engineering, Graduate School of Engineering,
Kobe University, Rokkodai, Nada, Kobe, 657-8501, Japan

Colloidal dispersions of semiconductor nanocrystals (NCs) can be used as “inks” for low-cost, solution-based deposition of films for optoelectronic applications. A common feature of colloidal NCs is capping of the surface with organic ligands which sterically or electrostatically stabilize NCs in solution. However, long organic ligands hinder charge carrier transport of films fabricated from these NCs. Processes for ligand removal or exchange in solution or during film formation have been employed. Unfortunately, these techniques cannot be applied to Si, because Si forms covalent bonds with organic ligands. We have recently developed a novel method to stabilize Si-NCs in solution without organic ligand passivation.[1] The strategy to attain solution dispersibility is heavy doping of B and P simultaneously on the surface of Si-NCs. The heavily B and P doped shell induces negative potential on the surface, which prevents agglomeration of NCs in polar solvents due to the electrostatic repulsion. In the presentation, I will discuss the results of structural characterization and photoluminescence properties of B and P codoped colloidal Si-NCs. I will also discuss the electrical transport properties of NC films produced from the colloid. [1] J. Phys. Chem. C 116, 17969 (2012), J. Phys. Chem. C 117, 6807 (2013), J. Phys. Chem. C 117, 11850 (2013).

Localized surface plasmon resonance of B- and P-doped Si nanocrystals

Xiaodong Pi

State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China

We have produced Si nanocrystals (NCs) that are rather heavily doped with B and P by means of a gas-phase approach [1]. It is found that localized surface plasmon resonance (LSPR) occurs to both B- and P-doped Si NCs [2,3]. We both experimentally and computationally show that the so-called Drude model traditionally used to describe the LSPR of noble metal NCs also works for the LSPR of semiconductor NCs if the dielectric screening and carrier effective mass of semiconductor NCs are considered. Significantly, electronic properties such as dopant activation and free carrier behavior can be elucidated by investigating the LSPR of doped Si NCs with the synergy of experiments and calculations. We clearly demonstrate that B-doped Si NCs are better positioned for the practical use of LSPR than P-doped Si NCs. The current findings may help advance the Si-NC-based plasmonics.

[1] S. Zhou, X. D. Pi, Z. Y. Ni, Q. B. Luan, Y. Y. Jiang, C. H. Jin, T. Nozaki, and D. Yang, *Particle and Particle Systems Characterization*, in press (2014).

[2] X. D. Pi and C. Delerue, *Physics Review Letters* **111**, 177402 (2013).

[3] S. Zhou, X. D. Pi, Z. Y. Ni, Y. Ding, D. Yang, C. Delerue and T. Nozaki, *submitted*.

Doping and characterization of impurity atoms in Si and Ge nanowires

N. Fukata¹, T. Sekiguchi¹, Y. Bando¹, K. Murakami², and Zhong Lin Wang³

1 National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Japan

2 Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan

3 School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

Silicon and germanium nanowires (SiNWs and GeNWs) are of great interest in the fields of both fundamental and application research. In this study, we investigated doping and their characterization in SiNWs and GeNWs.

SiNWs were synthesized by laser ablation and GeNWs were synthesized by CVD method. Micro-Raman scattering measurements were performed at room temperature with a 532-nm excitation light. Electron spin resonance (ESR) measurements were carried out at 4.2 K.

A Raman peak was observed at about 618 cm^{-1} for SiNWs synthesized by using a Si target with B. The peak frequency is in good agreement with that of a local vibrational mode of B in Si crystal. The Fano broadening due to a coupling between the discrete optical phonon and a continuum of interband hole excitations was also observed in the optical phonon peak, which indicates heavily B doping. The observation of B local vibrational peaks and Fano broadening were observed for the first time in our experiments [1,2]. These results prove that B atoms were doped in substitutional sites of the crystalline Si core of SiNWs [1,2]. ESR measurements were also performed to investigate defects and P donor/conduction electrons in P-doped SiNWs. The observation of ESR signal due to conduction electrons clearly showed that P atoms were doped in substitutional sites of the crystalline Si core of SiNWs [2,3]. The codoping of B and P were also investigated and the compensation effect in SiNWs was detected [4]. The segregation behaviors of B and P were investigated by using B local vibrational peaks and Fano broadening for B-doped SiNWs, while an ESR signal of conduction electrons was used for P-doped SiNWs. The results showed that the segregation of B is faster than that of P. Raman local vibrational peaks and Fano resonance due to B acceptors and P donors were also observed for B-doped and P-doped GeNWs, showing the formation of p-type and n-type GeNWs. The segregation of B and P were investigated for B-doped and P-doped SiNWs [5]. The results showed that the segregation of B is faster than that of P [6]. Recently, we also succeeded in growing Si/Ge and Ge/Si core-shell NWs and proving site-selective doping in Si/Ge and Ge/Si core-shell NWs [7].

References:

- [1] N. Fukata et al., *Appl. Phys. Lett.* **89** (2006) 203109. [2] N. Fukata, *Adv. Mater.* **21** (2009) 2829. [3] N. Fukata, *Appl. Phys. Lett.* **90** (2007) 153117. [4] N. Fukata et al., *Appl. Phys. Lett.* **93** (2008) 203106. [5] N. Fukata et al., *ACS NANO* **4** (2010) 3807. [6] N. Fukata et al., *NANO Lett.* **11** (2011) 651. [7] N. Fukata et al., *ACS NANO* **6** (2012) 3278.

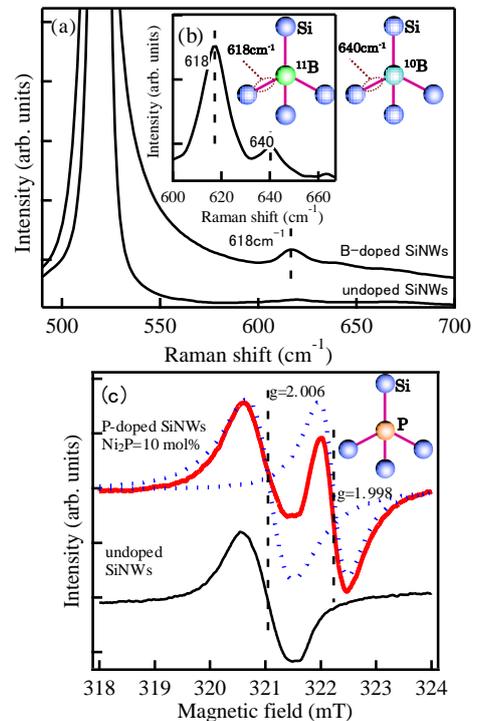


Fig. 1. (a) Raman spectra observed for B-doped and undoped SiNWs. (b) The magnification of (a). (c) ESR signals observed for P-doped and undoped SiNWs.

Challenges in work with nano-crystals in cell biology

Antonin Broz, Lucie Ostrovska, Marie Hubalek-Kalbacova

Institute of Inherited Metabolic Disorders, 1st Faculty of Medicine, Charles University Prague

Si nano-crystals (NC) are an alternative to quantum dots and organic fluorophores used in cell biology, histology and medicine for fluorescent staining. Before utilization of these fluorescent NC in biomedicine it is necessary to investigate their toxicity in vitro and fluorescence performance in biological environment. There are several challenges in work with NCs in biological experiments.

Well-defined colloid concentration and NC size enable determination of minimal concentration of NCs for suitable detection in microscope setups used for imaging in cell biology. It also allows to define correctly the toxicity of NCs. Closely related to the issue of NC colloid concentration is the quantum yield of NCs which should be as high as possible. The less living cell culture is illuminated the less stress the cells undergo during an experiment. The illumination issue is associated with the spectral characteristics of the NCs. UV light used for excitation of Si NCs can severely damage cell structures resulting in cell death. Another challenge in manipulation with NCs is their sterility and transportation conditions. Alcohols often used as a basis for NC colloids can prevent the colloid from bacterial infection and aggregation of NCs but they are also toxic for human cells. All these issues have to be addressed when preparing NCs for the biological experiments and it all places demands on cooperation and correct communication between physicists preparing NCs and cell biologists performing cell experiments.