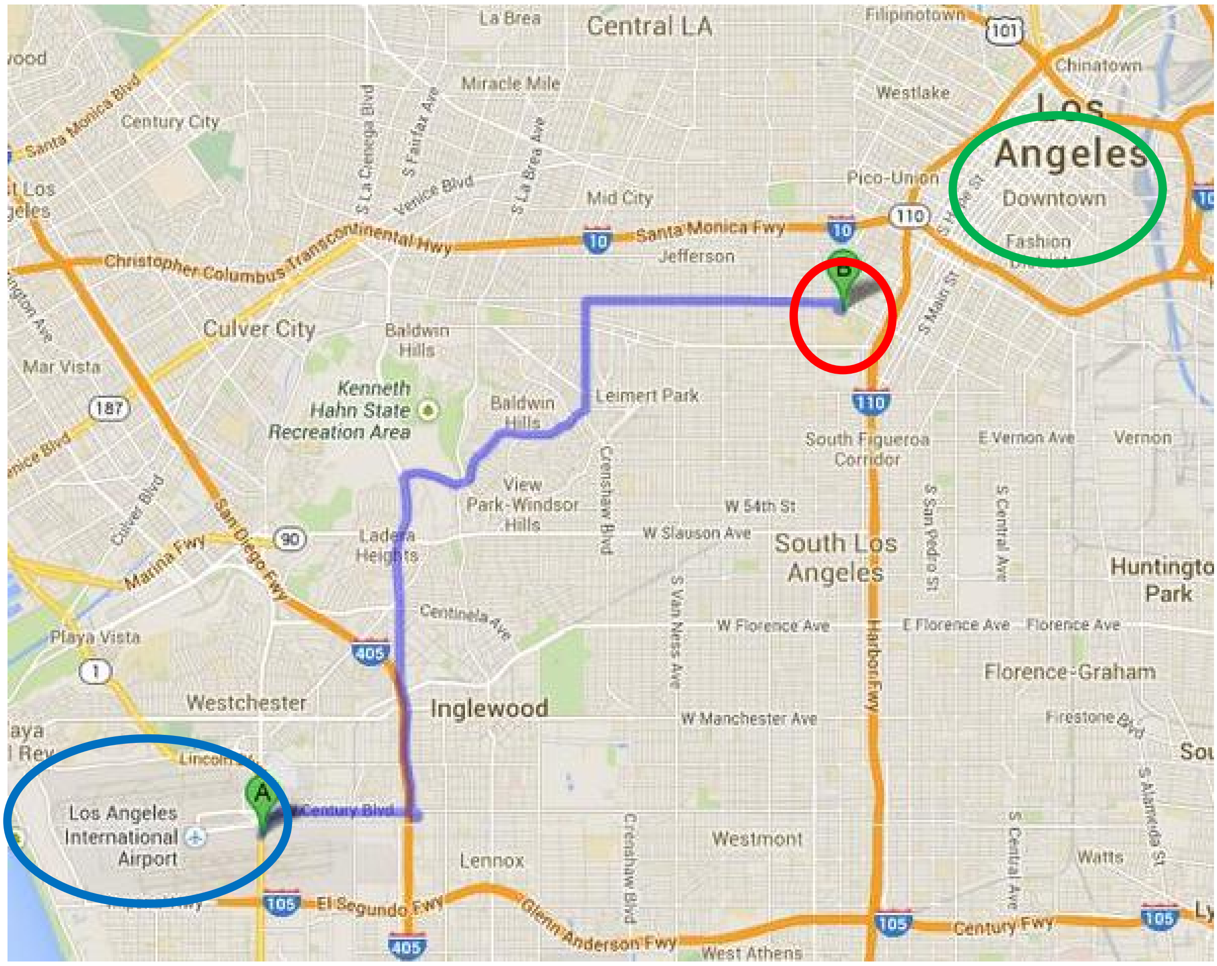
# Satellite Symposia for the *Fifteenth International Conference on the Science and Applications of Nanotubes*

June 1st and 7th 2014
University of Southern California
Los Angeles, California, USA

# Satellite Symposia Program

| | CCTN14 | MSIN14 | CNTFA14 | GSS14 |
|---|---|---|---|---|
| Location | EEB 132 | SLH 100 | SLH 102 | SLH 100 |
| Time | June 1 | June 1 | June 1 | June 7 |
| 9:00 | I1: Jerry Tersoff | K1: J Kono | K1: Mark Hersam | K1: J. Lau |
| 9:15 | | | | |
| 9:30 | | | | I1: K. Tsugakoshi |
| 9:45 | I2: Jerry Bernholc | I1: A. Balandin | I1: Yuan Chen | |
| 10:00 | | | | |
| 10:15 | | CT1: Subbaiyan | CT1: Bilu Liu | CT1: Artyukhov |
| 10:30 | (Coffee) Break | (Coffee) Break | (Coffee) Break | (Coffee) Break |
| 10:45 | | | | |
| 11:00 | CT1: Vasilii Artyukhov | I2: Stefan Strauf | I2: Jie Liu | I2: Wenjuan Zhu |
| 11:15 | | | | |
| 11:30 | CT2: Andrew T. Koch | CT2: A. Ishii | I3: Fei Wei | CT2: M. Neupane |
| 11:45 | | CT3: P. Finnie | | CT3: N. Perea |
| 12:00 | CT3: Zhen Zhu | I3: R. Bruce Weisman | I4: Andrea Ferrari | I3: A. Balandin |
| 12:15 | | | | |
| 12:30 | CT4: Jie Guan | CT4: J. Campo | CT2: A Sekiguchi | CT4: H-B. Li |
| 12:45 | | CT5: T. Uda | CT3: M Maeda | CT5: Vijayaraghavan |
| 13:00 | Lunch | Lunch | Lunch | Lunch |
| 13:15 | | | | |
| 13:30 | | | | |
| 13:45 | | | | |
| 14:00 | I3: Young-Woo Son | I4: H. Wang | I5: Ali Javey | K2: J. Hone |
| 14:15 | | | | |
| 14:30 | | CT6: Yomogida | I6: Lianmao Peng | |
| 14:45 | I4: Igor Bondarev | CT7: Yoshida | | I4: F. Withers |
| 15:00 | | I5: S. Maruyama | I7: T Takenobu | |
| 15:15 | | | | CT6: AbdelGhany |
| 15:30 | (Coffee) Break | (Coffee) Break | (Coffee) Break | (Coffee) Break |
| 15:45 | | | | |
| 16:00 | CT5: Takumi Araki | CT8: A. Loiseau | I8: Qingwen Li | I5: M. Blees |
| 16:15 | | CT9: R.Dhall | | |
| 16:30 | CT6: Hai-Bei Li | CT10: Bekyarova | I9: A Nasibulin | CT7: T. Susi |
| 16:45 | | I6: T. Saito | | CT8: I. Fakih |
| 17:00 | I5: Toma Susi | | I10: KL Jiang | CT9: M. Katkov |
| 17:15 | | I7: Y. Miyauchi | | I6: H-M. Cheng |
| 17:30 | | | CT4: Obraztsova | |
| 17:45 | Closing remarks | Closing remarks | Closing remarks | Closing remarks |
| 18:00-20:00 | Welcome Reception | Welcome Reception | Welcome Reception | |

# Map of Los Angeles

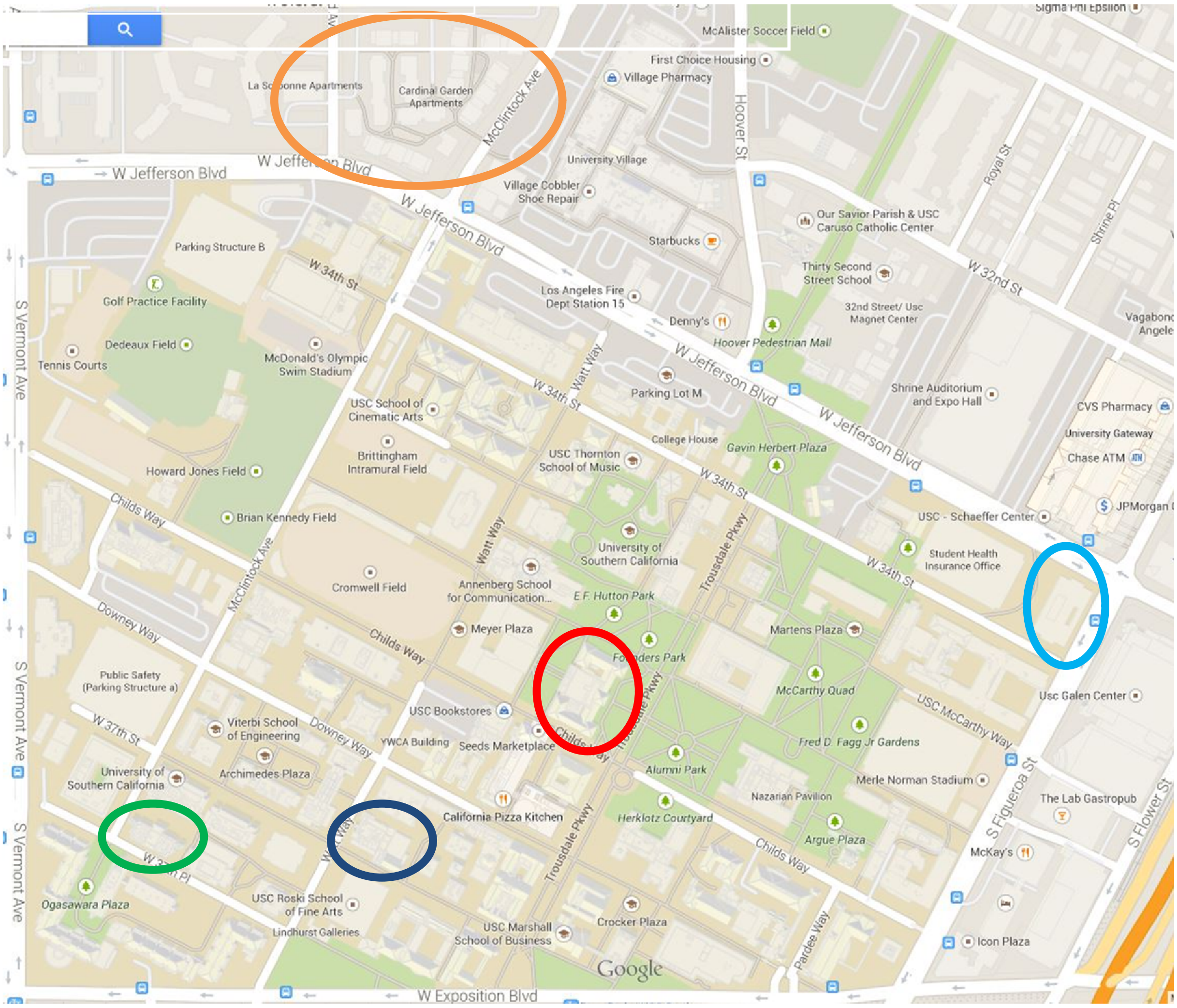


University of Southern California

Downtown Los Angeles

Los Angeles International Airport (LAX)

# USC Campus Map



**Bovard Auditorium (ADM)**
**3551 Trousdale Parkway**

**Cardinal Gardens (CAR)**
**3131 McClintock Avenue**

**Davidson Conference Center (DCC)**
**3415 South Figueroa Street**

**Stauffer Science Lecture Hall (SLH 100, SLH102)**
**831 Bloom Walk**

**Hughes Aircraft Electrical Engineering Center (EEB 132)**
**3740 McClintock Ave.**

# CCTN14: Ninth International Symposium on Computational Challenges and Tools for Nanotubes

**Sunday June 1, 2014**
EEB 132
3740 McClintock Ave.
Los Angeles, CA

**CCTN14 Organizers**

Steven G. Louie
(University of California at Berkeley, USA)
Hisashi Nakamura
(Research Organization for Information Science & Technology (RIST) Tokyo, Japan)
David Tomanek
(Michigan State University, USA)

## Scope

This satellite symposium of the NT14 conference focuses on quantitative understanding of unique physical properties of nanotube systems using advanced computational approaches. We will highlight the computational challenges in modeling these systems and discuss new tools to master these challenges. We intend to feature significant advances in theoretical understanding, in computational approaches and algorithms, as well as new hardware, including the upcoming generation of high-performance computers, capable of tackling these challenges.

**Invited speakers**

Jerry Tersoff
(IBM Yorktown Heights)
Jerry Bernholc
(North Carolina State University)
Young-Woo Son
(Korea Institute for Advanced Study)
Igor Bondarev
(North Carolina Central University)
Toma Susi
(University of Vienna, Austria)

**I1**

# Scaling of Metal-Nanotube Contacts

Jerry Tersoff, Vasili Perebeinos

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For carbon nanotube transistors to compete with silicon, they must be integrated with very high device density. This route is being actively pursued, but there are challenges in scaling devices to the required size and spacing. Perhaps the most important, and least understood, is the transfer length over which electrons transfer from the metal to the nanotube. Devices with contacts much shorter than this transfer length have proportionally increased contact resistance. Unfortunately, the measured length is surprisingly long, roughly 100nm, much larger than the desired contact lengths. We predict that the transfer length under realistic device conditions is actually much shorter than the measured value, because the transfer length shrinks with decreasing tube diameter and increasing bias voltage. The physical mechanisms will be discussed.

Device integration also requires closely-spaced arrays of tubes, with several tubes per device, to give adequate drive current. We find that with scaling of the tube spacing toward smaller pitch, there is a structural transition to a geometry in which the metal poorly wets the nanotube and substrate. This gives a sudden decrease in contact adhesion, and probably also an increase in contact resistance. Several interesting aspects of the wetting geometry will be discussed.

**I2**

# Electronic Structure and Electron Transport in Carbon-Based Nanosystems

Jerry Bernholc

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The development of molecular-scale devices and circuits can be significantly enhanced by predictive simulation and by formulating generic principles that will aid in their design. This talk describes three recent examples: (i) We discuss the electronic structure and spin polarization of nitrogen-doped carbon nanoribbons, which are candidate materials for ultrahigh speed electronics. It turns out that only certain classes of nearly perfect nanoribbons are suitable for devices. (ii) We investigate electron transport in DNA and the effects of base-pair matching, solvent and counterions. All of these dramatically affect the conductivity of the system, which explains the wide range of results observed experimentally. (iii) We consider molecular sensors based on carbon nanotubes and describe configurations based both on direct attachment (physisorption and chemisorption) and indirect functionalization via covalent and non-covalent linkers.

In collaboration with Y. Li, B. Tan, J. Jiang, M. Hodak, W. Lu and P. Boguslawski.

**I3**

# Interactions in interlayer spaces of layered materials

Young-Woo Son

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Many layered materials such as multilayered graphene, BN, and $MoS_2$ have distinct physical and chemical properties related with interactions between layers. In this work, I will present our recent theoretical works related with delicate interactions between layers themselves and with inserted liquids in interlayer spaces. First, depending on characteristics of layer interactions, it is shown that the responses of layered materials to external mechanical forces vary greatly ranging from weakly compressible, completely compressible to auxetic spacing variations [1]. Second, when water can immerse into interlayer spaces of graphene oxide, the formation of ice layers and their dislocations are shown to depend on interlayer distances critically [2], which may provide a clue to explain a recent experiment [3] on the peculiar water dynamics in graphene oxide.

[1] S. Woo and Y.-W. Son, in preparation.
[2] D. W. Bouhkvalov, M. I. Katsnelson, Y.-W. Son, Nano Lett. 13, 3930 (2013).
[3] R. R. Nair et al, Science 335, 442 (2012)

**I4**

# Relative stability of excitonic complexes in quasi-one-dimensional semiconductors

Igor Bondarev

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The (asymptotically exact) Landau-Herring approach [1,2] that was first implemented earlier in Ref.[3] to evaluate the biexciton binding energy in small-diameter carbon nanotubes (CNs), is now used to derive a universal asymptotic relationship between the lowest energy trion (charged exciton), biexciton and exciton binding energies in quasi-one-dimensional (1D) semiconductors. The model operates in terms of the under-barrier tunneling current between equivalent configurations of the system in the configuration space. It allows one to interpret theoretically and thus to understand some important relative stability peculiarities of neutral and charged exciton complexes in quasi-1D systems, such as why in semiconducting quantum wires the positive trion binding energy is less than the biexciton binding energy [4,5], whereas in CNs the binding energy of the trion (negative or positive) is greater than that of the biexciton [6-8]. For CNs with diameters ~1 nm, the model predicts the trion binding energy greater than that of the biexciton by a factor ~1.4 decreasing with the diameter, in reasonable agreement with the latest non-linear spectroscopy measurements of Refs.[7,8] [1.46 for the (6,5) CN and 1.42 for the (9,7) CN, respectively].

This research is supported by the US Department of Energy (DE-SC0007117).

[1] L.D. Landau and E.M. Lifshitz, Quantum Mechanics (Pergamon, Oxford, 1991).
[2] C. Herring, Rev. Mod. Phys. 34, 631 (1962).
[3] I.V. Bondarev, Phys. Rev. B 83, 153409 (2011).
[4] B. Szafran, et al., Phys. Rev. B 71, 235305 (2005).
[5] H. Zhang, M. Shen, and J.-J. Liu, J. Appl. Phys. 103, 043705 (2008).
[6] R. Matsunaga, K. Matsuda, and Y. Kanemitsu, Phys. Rev. Lett. 106, 037404 (2011).
[7] B. Yuma, et al., Phys. Rev. B 87, 205412 (2013).
[8] L. Colombier, et al., Phys. Rev. Lett. 109, 197402 (2013).

**I5**

# Silicon-carbon bond inversions driven by 60 keV electrons in graphene

Toma Susi, Jani Kotakoski, Demie Kepatsoglou, Clemens Mangler, Tracy C. Lovejoy,
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Single-layer graphene is arguably an ideal material for atomic resolution electron microscopy. But even in the so-called 'gentle' conditions used for atom-by-atom investigations, beam damage effects cannot be neglected. Imperfections such as doping also change the effect an electron beam has on the atomic structure of graphene, as we have recently shown for nitrogen substitutions [1].

We now demonstrate that 60 keV electron irradiation drives the diffusion of threefold coordinated Si dopants in graphene by one lattice site at a time [2]. First principles molecular dynamics simulations reveal that each step is caused by an electron impact on a C atom next to the dopant. Although the atomic motion happens below our experimental time resolution, stochastic analysis of 38 such lattice jumps reveals a probability for their occurrence in a good agreement with the simulations.

Conversions from three- to fourfold coordinated dopant structures and the subsequent reverse process are significantly less likely than the direct bond inversion. Our results thus provide a model of non-destructive and atomically precise structural modification and detection for two-dimensional materials.

[1] T. Susi, J. Kotakoski, R. Arenal, S. Kurasch, H. Jiang, V. Skakalova, O. Stephan, A. V. Krasheninnikov, E. I. Kauppinen, U. Kaiser, and J. C. Meyer, ACS Nano 6, 8837 (2012).
[2] T. Susi et al., submitted (2014)

**CT1**

# Carbyne: The physics of one-dimensional carbon

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We investigate the physical properties of carbyne using first principles calculations. Under tension, carbyne displays an extreme stiffness, beating all known materials in specific stiffness and strength. With respect to bending, despite its one-atom thickness, carbyne behaves as a stiff rod at length scales below its persistence length ~ 14 nm (room temperature). The cylindrical symmetry of carbyne makes it a challenge to define a torsional deformation but can be broken via attachment of "handles" at the chain ends, whereupon the chemical nature of these handles determines whether they will rotate freely or if the system will behave as a beam with a finite tensile stiffness. Based on these three fundamental deformations we produce a comprehensive equivalent continuum-mechanics representation for carbyne [1]. Mechanical deformations also have a profound effect on the electronic properties of carbyne [2]. Under tension, the Peierls dimerization of carbyne (responsible for the symmetry-breaking transition from metallic cumulene phase to dielectric polyyne) quickly increases, and so does the band gap. We explain this unusual phenomenon using a simple yet general analytical model, applicable to all Peierls systems. We also find that stretching strongly affects the transport properties of carbyne, decreasing the mobility as the electron–phonon coupling gets enhanced—however, due to an unusually low effective mass, the mobility remains high compared to conventional materials. By further adding the quantum zero-point motion of atoms into the picture, we show how the Peierls ground state gets destabilized in free carbyne, restoring the metallic cumulene structure, yet a moderate stretching reverses the balance, causing a tension-driven metal–dielectric transition. In another mode of deformation, twisting a carbyne chain with $sp^2$ handles by 90 degrees causes a singlet–triplet spin transition. This combination of carbyne′s unique electro/opto-mechanical properties entails many interesting applications in nanoscale mechanical, electronic, and spintronic components, which however rely on the chemical stability of carbyne. To investigate this aspect, we analyze the carbyne–carbyne cross-linking reaction [1, 3] to estimate the possible lifetime of this material.

[1] M. Liu, V.I. Artyukhov, H. Lee, F. Xu, and B.I. Yakobson, ACS Nano 7, 10075 (2013).
[2] V.I. Artyukhov, M. Liu, and B.I. Yakobson, arXiv:1302.7250
[3] G. Casillas, A. Mayoral, M. Liu, A. Ponce, V.I. Artyukhov, B.I. Yakobson, and M. Yacaman, Carbon 66, 436 (2014).

**CT2**

# Graphenylene-based nanotubes

Andrew T. Koch, Saloome Motavas, Harrison D. E. Fan, Amir H. Khoshaman, George Sawatzky, Alireza Nojeh

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The electronic properties of a new type of carbon nanotube based on the graphenylene motif were investigated using density functional and tight-binding methods. The structure of a graphenylene nanotube consists of six-membered as well as four-membered rings of $sp^2$ carbon atoms, with localized pi bonds fixed around the six-membered rings. As a result, these nanotubes exhibit three distinct bond lengths between carbon atoms. They also possess unique dodecagonal pores with ~5.4 Å diameter. Analogous to conventional graphene-based carbon nanotubes, a two-dimensional graphenylene sheet can be “rolled” into a seamless cylinder in armchair, zigzag, or chiral orientations. The resulting nanotube can be described using the familiar (n,m) nomenclature. Density functional theory-based calculations predict zigzag graphenylene nanotubes to be small bandgap semiconductors, with an increasing bandgap as the diameter decreases. Similar to traditional carbon nanotubes, zigzag graphenylene nanotubes with indices mod(n-m,3)=0 exhibit a smaller bandgap than other zigzag graphenylene nanotubes with comparable diameters. Interestingly, density functional calculations predict metallic behavior for armchair graphenylene nanotubes with small diameters (< 13 Å), and semiconducting behavior with a small bandgap for armchair graphenylene nanotubes with larger diameters.

[1] J. M. Soler et al. J. Phys.: Condens. Matter 14 2745 (2002)
[2] D. Porezag, T. Frauenheim, T. K. Kohler, G. Seifert, R. Kaschner, Phys. Rev. B 51, 12947−12957 (1995)
[3] G. Brunetto et al. J. Phys. Chem. C, 116, 12810-12813 (2012)
[4] Q. Song et al. J. Mater. Chem. C, 1, 38 (2013)

**CT3**

# Spontaneous origami in multi-phase 2D phosphorus

Zhen Zhu, Jie Guan, David Tomanek

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Similar to graphitic carbon, phosphorus monolayers, dubbed phosphorene [1], can be exfoliated from layered black phosphorus. Phosphorene is a p-type semiconductor with a significant band gap. It is stable, flexible, and displays a high carrier mobility [1], suggesting its potential use in 2D electronics. Most interesting, based on ab initio density functional calculations, we found that phosphorus can form four different 2D structural phases that are almost equally stable and may be inter-connected. Connection of two planar phases resembles a sharp origami-style fold. This fold occurs naturally in this multi-phase system, whereas in single-phase systems like graphene it requires the presence of defect lines or lines of adsorbed atoms. We also find the possibility of moving this fold by structural transformation from one allotrope to another, with an unusually low activation barrier of <0.5 eV per bond. Since the electronic properties of multi-phase phosphorene may also be tuned by in-layer strain, including a semiconductor-to-metal transition, we postulate that origami-style folded phosphorene should display an unprecedented richness in its electronic behavior.

[1] H. Liu et al. ACS Nano 8 (2014)
[2] Z. Zhu and D. Tomanek, Phys. Rev. Lett. (2014)

**CT4**

# Polygonal nanotubes of multi-phase layered phosphorus

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Similar to graphite, black phosphorus is a layered structure that can be exfoliated to monolayers dubbed phosphorene[1]. Similar to carbon nanotubes, which are related to few-layer graphene, we propose the existence of phosphorus nanotubes formed of phosphorene, Different from graphite, besides the black allotrope, layered phosphorus has three stable structural phases, called blue-P [2], γ-P and δ-P, which can be connected naturally. The fact that connected structures do not lie in a plane allows us to design nanotubes by connecting laterally nanoribbons of different phases. Unlike single-phase nanotubes consisting of a layer rolled up to a cylinder, multi-phase phosphorene nanotubes will have a polygonal cross-section.

Both single-wall and multi-wall phosphorene nanotubes may be constructed in this way. The availability of more than one structural phase offers much larger structural richness than the carbon counterpart with one single phase. Consequently, we find that the electronic properties of phosphorene nanotubes depend not only on the chiral vector that defines the edge structure, but also the presence of the individual phosphorene phases. In analogy to the successful synthesis of carbon nanotubes by ball milling of graphite, we believe that phosphorene nanotubes may be formed in the same way in an inert atmosphere.

[1] H. Liu et al. ACS Nano 8 (2014)
[2] Z. Zhu and D. Tomanek, Phys. Rev. Lett. (2014)

**CT5**

# The influence of the curvature of surface and π electrons on adsorption of nanocarbons

Takumi Araki, Syogo Tejima, Shatoshi Nakamura, Hisashi Nakamura, David Tomanek, Morinobu Endo

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Nano carbons structures as CNTs, graphenes, fullerene, Mackay crystal and their composite have been attracting scientists and engineers to finding of novel functional materials for water technology and electronics.

We have investigated the adsorption of nanocarbons as adsorbent with varying their surface curvature at adsorption point by use of ab initio simulation.

The adsorption of CNTs, fullerene, graphene and Mackay crystals, has been simulated for Cesium, Cs, as adsorbate. The results show commonly that π-electron extending beyond the surface of carbons plays important role for catching the valence 6s electron of alkali metal Cs. The valence 6s electron of Cs flows into nanocarbon's π orbitals. It helps for nanocarbons to adsorb Cs stably by the charge transfer interaction. The surface curvature of the adsorption point clearly influences on the adsorption strength. The adsorption becomes more stable if curvature radius of CNTs increases. For the negative Gaussian curvature of Mackay crystals, the adsorption is enhanced around octagonal rings among the hexagons. This result points out that such a sophisticated configuration by the spread of π electrons contributes to the adsorption strength.

The feature is useful for nanocarbon filter or film in novel water technology or future carbon electronic materials.

**CT6**

# SWCNT Growth from Organic Precursors Without a Catalyst: Possibilities and Limitations Revealed by Theoretical Simulations

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Our recent simulations of catalyst-free, chirality-controlled growth from cycloparaphenylene (CPP) precursors are presented. We will show that different chemical routes for chirality-controlled growth exist, and depend on the nature of the growth agent. We demonstrate this phenomenon using acetylene ($C_2H_2$) and the ethynyl radical ($C_2H$) as growth agents, at temperatures ranging from 300 to 800 K. In the case of the ethynyl radical, we observe a strong dependence of the SWCNT growth rate on the chiral angle. This is consistent with a previously proposed screw-dislocation-like model of transition metal-catalyzed SWCNT growth. However, the absence of a catalyst in this case indicates that the SWCNT growth rate is an intrinsic property of the SWCNT edge itself. Additionally, the ability of a SWCNT to avoid defect formation during growth is also an intrinsic quality of the SWCNT edge, one that is maximized at lower temperatures. However, using the ethynyl radical as the growth agent, the SWCNT diameter does not influence the growth rate; acetylene-based growth is, on the other hand, strongly diameter-dependent. We therefore predict the existence of a maximum local growth rate for a particular (n,m) SWCNT at a given acetylene/ethynyl ratio.

# MSIN14: Eighth International Workshop on Metrology, Standardization and Industrial Quality of Nanotubes

**Sunday June 1, 2014**
SLH 100
831 Bloom Walk
Los Angeles, CA

**Organizers**

Ming Zheng
Ado Jorio
Hiro Kataura
Mildred Dresselhaus
Stephen B. Cronin

## Scope

This satellite symposium is dedicated to the metrology, standardization and industrial quality of carbon nanotubes and related materials. Adoption of a new material in industry requires consistency and quality that can only be assured by international standards of measurement. The research community also benefits from standard measurement practices and quality in carbon nanotubes as it facilitates inter-laboratory comparisons of research results. Development of protocols for the definition of sample parameters like composition, purity, stability, homogeneity, dispersability, structural metrics are keys for both research and applications of nanotubes and graphene. The MSIN13 workshop strives to bring together the international stakeholders in measurement science and standardization to build consensus on best measurement practices to assure consistency and quality in the field of carbon nanotubes and graphene.

**Invited Speakers**

Alexander Balandin
Han Wang
R. Bruce Weisman
Stefan Strauf
Shigeo Maruyama
Junichiro Kono
Motoo Yumura

**I1**

# Low-Frequency Current Fluctuations and 1/f Noise in Graphene

Alexander A. Balandin

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Low-frequency current fluctuations with the spectral density S(f)~1/f (f is the frequency) is a ubiquitous phenomenon observed in a wide variety of electronic materials and devices. This type of fluctuations, referred to as 1/f noise dominates the spectrum at frequency below 100 kHz. Low-frequency 1/f noise limits the sensitivity of sensors and makes the main contribution to the phase-noise of communication systems via its up-conversion. It is now accepted that different fluctuation processes can be responsible for 1/f noise in various materials and devices. For this reason, practical applications of every new material system require a thorough investigation of specific features of the low-frequency noise in this material and developing methods for its reduction. It has already been demonstrated that the low-frequency current fluctuations in graphene [1-3] and thin films of van der Waals materials [4] reveal unusual gate bias dependence, which cannot be described with conventional Hooge parameter or McWhorter model. In this talk, I will review state-of-the-art in the 1/f noise field in graphene and van der Waals materials, and describe possibilities for deeper understanding of 1/f noise offered by availability of continuous atomically thin films. A long-standing question of importance for electronics is whether 1/f noise is generated on the surface of conductors or inside their volumes. Using graphene multilayers we were able to directly address this fundamental problem of the noise origin. Unlike the thickness of metal or semiconductor films, the thickness of graphene multilayers can be continuously and uniformly varied all the way down to a single atomic layer of graphene – the actual surface. We found that 1/f noise becomes dominated by the volume noise when the thickness exceeds ~7 atomic layers (~2.5 nm). The 1/f noise is the surface phenomenon below this thickness [5]. We investigated experimentally the effect of the electron-beam irradiation on the level of the low-frequency 1/f noise in graphene devices. It was found unexpectedly that 1/f noise in graphene reduces with increasing concentration of defects induced by irradiation [6]. The bombardment of graphene devices with 20-keV electrons reduced the noise spectral density by an order-of magnitude at a certain radiation dose [6-7]. The noise reduction can be explained within the mobility fluctuation mechanism. The obtained results are important for the proposed applications of graphene in sensors and communications [7].

[1] G. Liu, et al., Appl. Phys. Lett., 95, 033103 (2009);
[2] S. Rumyantsev, et al., J. Phys.: Cond. Matter, 22, 395302 (2010);
[3] G. Liu, et al., Appl. Phys. Lett., 100, 033103 (2012);
[4] M.Z. Hossain, et al., ACS Nano, 5, 2657 (2011);

[5] G. Liu, et al., Appl. Phys. Lett., 102, 093111 (2013);
[6] M. Z. Hossain, et al. Appl. Phys. Lett., 102, 153512 (2013);
[7] A.A. Balandin, Nature Nanotechnology, 8, 549 (2013).

**I2**

# Intrinsic regime of exciton emission in ultra-clean carbon nanotubes bridging an air gap

Stefan Strauf[1], Ibrahim Sarpkaya[1], Zhengyi Zhang[2], William Walden-Newman[1], Xuesi Wang[2], James Hone[2], Chee-Wei Wong[2]

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The photophysics of excitons in single-walled carbon nanotubes has been the subject of much recent interest. While large exciton binding energies are promising for optoelectronic devices, photoluminescence quantum yields are rather low due to dominant extrinsic nonradiative recombination of highly mobile excitons exploring defects and dopants along the tube. As a result, spontaneous emission lifetimes ($T_1$) of 20-200 ps, ultrafast exciton dephasing times ($T_2$) of about 500 fs, and spectral linewidth of several meV characterize the exciton emission in most experiments. The question arises to what extend previous experiments probe for the true intrinsic properties of the exciton dynamics and how one could reach deeper into the intrinsic regime. To this end we have studied ultra-clean carbon nanotubes bridging an air gap over pillar posts [1]. Our measurements demonstrate the onset of a new regime of intrinsic exciton photophysics with prolonged spontaneous emission times up to $T_1$=18 ns, in agreement with values first hypothesized by theorists about a decade ago [2]. Furthermore, we measure for the first time the exciton decoherence times of individual nanotubes in the time-domain and found four-fold prolonged values up to $T_2$=2.1 ps compared to ensemble measurements. In addition, the exciton emission displays narrow spectral linewidth down to 220 eV, which have recently also been independently confirmed and surpassed with even lower values down to 40 eV [3]. These first observations of an intrinsic exciton photophysics regime in single-walled carbon nanotubes motivate new discussions about the magnitude of the intrinsic dephasing mechanism while the observed prolonged exciton dynamics and improved quantum yields are promising news for photonic device applications.

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**I3**

# Advanced Spectrometric Characterization of Single-Walled Carbon Nanotube Samples

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Many important photophysical properties of SWCNTs remain inadequately determined, including (n,m)-specific absorption cross sections, emissive quantum yields, and fluorescence action cross sections. A major challenge has been quantifying structure-specific SWCNT concentrations in dispersed mixed samples. We have used short-wave IR fluorescence microscopy to image and count individual nanotubes within known volumes of structurally sorted samples, thereby directly finding (n,m)-specific particle concentrations. Separate measurements of the length distribution and bulk absorbance then give absolute absorption cross sections per SWCNT carbon atom. We find cross sections that are inversely related to nanotube diameter. $E_{11}$ cross sections are larger for mod 1 species than for mod 2, whereas the opposite pattern is found for $E_{22}$ transitions.

We also introduce a new experimental method, Spectral Analysis of Fluorescence Fluctuations (SAFF). Here, long sequences of millisecond-scale emission spectra are captured from dispersed SWCNT samples that are dilute and thin enough to show clear intensity variations reflecting statistical variations in the numbers of nanotubes inside the small probed volume. In contrast to normal fluorescence correlation spectroscopy, our method is spectrally resolved. The fluctuation data are analyzed to reveal relative abundances of (n,m) species, isolate emission spectra of single species, show inhomogeneous spectral components, and expose the presence of small SWCNT aggregates (through spectral cross-correlations).

**I4**

# Rediscovering Black Phosphorus: A Unique Anisotropic 2D Material for Optoelectronics and Electronics

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Anisotropy refers to the property of a material exhibiting directionally dependent features. In this work, we introduce black phosphorous (BP), the most stable allotrope of phosphorus in layered orthorhombic structure with a bandgap of 0.3 eV in bulk, as a unique elemental 2D material in which electrons, phonons and their interactions with photons behave in a highly anisotropic manner within the plane of the layers. The unique anisotropic nature of BP thin films is revealed using angle-resolved Raman and infrared spectroscopies, together with angle-resolved transport study. For 15 nm thick BP, we measure Hall mobility of 1000 and 600 $cm^2/Vs$ for holes along the light (x) and heavy (y) effective mass directions, respectively, at 120 K. These BP thin films also exhibit large and anisotropic in-plane optical conductivity from 2 to 5 µm wavelength. Field effect transistors using 4 to 30 layers of BP (2 to 15 nm) as channel material exhibit an on-off current ratio exceeding 105, a field-effect mobility of 205 $cm^2/Vs$, and good saturation properties all at room temperature, suggesting its promising future in high performance thin film electronics. By introducing narrow bandgap BP into the 2D material family, we fill the space between semi-metallic graphene and large bandgap transition metal dichalcogenides (TMDCs), where great potentials for infrared optoelectronics lie. Most importantly, the unique anisotropic nature of this intriguing material creates unprecedented possibilities for the realization of conceptually new optoelectronic and electronic devices in which angle-dependent physical properties are highly desirable. I will conclude with remarks on how this unique 2D material is expected to bring new opportunities for novel applications in nano-electronic and nano-photonic systems.

**I5**

# Nitrogen-Incorporated Single-Walled Carbon Nanotubes for Devices

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We synthesized single-walled carbon nanotubes (SWNTs) with small diameter and narrow diameter distribution using acetonitrile (AcN)-mixed ethanol (EtOH) feedstock. Due to the presence of nitrogen (N) during synthesis, the SWNT mean diameter was dramatically reduced from approximately 2.1 nm to less than 1 nm as AcN was added as carbon source [1, 2]. Surprisingly, the main nitrogen configuration was found to be encapsulated diatomic $N_2$ molecules interior of SWNTs with the content of 1 at % [3, 4]. As the sequence of feedstock was switched during synthesis, SWNT diameter was changed along the vertically aligned array. A majority of nanotube junctions between two different diameter nanotubes were found to be discontinuous, while a minority of continuous junctions were revealed by high-resolution transmission electron microscope[5]. This diameter modulation was reversible upon the sequence of feedstock introduction. Additionally, the observed $N_2$ molecules on the top of double-layered SWNT vertical array, where the top layer was EtOH-grown array, imply that encapsulated $N_2$ molecules were migrating across nanotube junctions, indicating a viability of connected SWNTs with different diameters. We also address the role of nitrogen on influencing the SWNT diameter in which nitrogen affects only the surface of the catalyst particle, resulting in a change from the Octopus to the VLS growth mode, which results in a smaller diameter. Several devices using this nitrogen-incorporated SWNTs will be discussed.

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**I6**

# Structures of Carbon Nanotubes; their Controllability and Characterization

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Since the properties of carbon nanotubes (CNTs) strongly depend on their structures [1], methods for synthesis of CNTs with precisely controlled structures are essential for many of their possible technological applications. Therefore, syntheses for CNTs with controlled structures are required in addition to mass production methods. Chemical vapor deposition (CVD) methods have been the subject of considerable research efforts [2], because they can concurrently satisfy both the mass production and structural control requirements for CNT synthesis. Extensive studies have been performed on structural control in CVD synthesis of CNTs in terms of their number of layers [3], diameter [4], length [5], and chirality [6] by modifying the various catalysts, substrates, carbon sources, and precursors used.

We have developed a novel floating-catalyst CVD method with precise diameter-controllability called enhanced direct injection pyrolytic synthesis (eDIPS) [4] in which at least two kinds of hydrocarbons with different decomposition properties are used as carbon sources. Because of their high throughput and productivity [7], floating-catalyst CVD methods such as eDIPS-CVD are some of the most suitable CVD processes for the industrial production of CNTs with the high quality (degree of graphitization). TEM observation and optical absorption spectroscopy suggested that the mean diameter of single-wall CNTs produced by eDIPS-CVD was selectively tuned at any point within the range ca. 1.0 nm to 2.0 nm [4,8]. The photoluminescence mapping and optical absorption spectroscopy showed the dominant chirality of (7,5) in the narrower eDIPS-SWCNTs [9]. On the other hand, we have also reported that the tube length can be controlled by cross-flow filtration [10] or the way of dispersing [11]. Furthermore, it has been revealed that eDIPS-CVD with toluene as a primary carbon source and pyrolytically stable methane as a secondary carbon source provides the preferential growth of double-walled (DW) CNTs[12]. At the symposium, we will also show the properties of the commercialized eDIPS-SWCNTs, because recently industrial production plant of eDIPS-CVD was developed and high-quality, high-purity SWCNTs synthesized in this plant has been introduced to the market in 2014. The author wishes to acknowledge the financial

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## I7

# Photophysics of Carbon Nanotubes with Local Luminescent States

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Semiconducting single-walled carbon nanotubes exhibit near infrared luminescence[1], and their emission photon wavelengths are suitable for photonic applications in telecommunication, quantum information, and bio-imaging technologies. However, relatively low quantum yield of free exciton luminescence typically on the order of 10-3 – 10-2 [1-3] has limited such applications of carbon nanotubes. In this context, recently, fabrication and characterization of local luminescent states in carbon nanotubes have attracted much attention because of the enhanced photoluminescence in such local states promising for applications as near-infrared light emitters [4-9]. In order to evaluate and compare luminescence properties of various kinds of local states in carbon nanotubes, determination of luminescence quantum yields of a single localized exciton is essential. We will discuss how the luminescence quantum yield of a localized exciton in carbon nanotubes can be evaluated [6]. Moreover, we will report observation of strong nonlinear photoluminescence saturation from such local states; the phenomenon is attributed to unique exciton dynamics in one-dimensional nanostructures with sparse local states, as verified by Monte Carlo simulations of exciton diffusion dynamics.

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**CT1**

# Surfactant's Key Role in Aqueous two-phase Separation of Carbon Nanotubes: Toward Simple Chirality Isolation

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Aqueous two-phase extraction has recently been demonstrated as a new method to separate single-wall carbon nanotubes (SWCNTs) by diameter/chirality.[1] The separation is based on the relative hydrophobicity of the SWCNTs. In this paper, we will demonstrate that this hydrophobicity can be tuned by the exact surfactant composition at the SWCNT-surface.[2] By strategically combining multiple surfactants with different diameter-dependent binding affinities for SWCNTs and salts that readjust the surfactant structure within the mixed micelle surrounding the SWCNTs, we developed a simple, easily scalable and extremely fast method for obtaining highly enriched single-chirality suspensions in just 1 or 2 steps.

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**CT2**

# Exciton diffusion and related decay processes in individual air-suspended carbon nanotubes

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We investigate exciton diffusion, end quenching, and exciton-exciton annihilation processes in individual air-suspended carbon nanotubes by photoluminescence microscopy [1]. We have performed excitation spectroscopy on thousands of nanotubes to identify their chiralities and filter out bundles. In such a large dataset, we observe slightly redshifted satellite peaks which suggest the existence of single chirality bundles. Intrinsic exciton diffusion lengths for six different chiralities are obtained by analyzing the length dependence of emission intensity with a random walk theory [2,3]. We also estimate absorption cross sections by comparing the power dependence with Monte Carlo simulations, and inspired by the agreement, we have obtained an analytical expression that reflects the one-dimensional nature of exciton diffusion.

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**CT3**

# Raman spectroscopic metallicity figures of merit for metrological assessment of single walled carbon nanotube ensembles

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For electronic applications it is useful to control the single walled carbon nanotube (SWCNT) type (metal or semiconductor) precisely and accurately. Pure materials are now readily available, and while there are many ways to distinguish between metallic and semiconducting nanotubes, it remains a metrological challenge to practically assess "metallicity", especially in highly pure samples, in bulk. As the Kataura plot shows, metal and semiconductor SWCNTs have distinct optical resonances and they have distinct Raman spectra. Therefore a common approach is to use Raman spectroscopy to characterize metallicity. However, there are various possible procedures. A metric should be clearly prescribed, reproducible, and quantitative, and ideally, easy to apply. Here I will describe the testing of two Raman spectroscopy derived metallicity figures of merit against commercially available metal rich and semiconductor rich materials of various purities, both liquid and solid, as well as non-commercial polyfluorene sorted nanotubes. These are compared to absorption based figures of merit. The Raman scattering cross-section and the resonant excitation profile are critical to metrological assessment of metallicity. A meaningful and precise Raman metallicity figure of merit can be obtained quickly and easily with a sensitivity relevant to currently accessible purities. However, there are practical limitations to simple metallicity figures of merit, and these and more fundamental limits associated with such approaches will be described.

**CT4**

# Optical characterization of the filling of carbon nanotubes with organic molecules

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Recent progress in carbon nanotube (NT) research has allowed the synthesis of various organic-NT hybrids, creating a critical need for dedicated characterization techniques of such complex systems. Solubilization of NTs with bile salt surfactants[1] has enabled major advances in their processing, purification, and in particular their spectroscopic study. The regular, unperturbing coating yields much narrower spectral linewidths than other surfactants, allowing to resolve the spectroscopic features of e.g. empty (closed) and water-filled NTs, even for the very thinnest tubes, where only a single file of water molecules fits inside the nanotube channel.[2-5] Also the filling with larger organic molecules results in very specific spectroscopic changes to both the NTs and the encapsulated molecules. We will show how energy-transfer from the molecules to the NTs, and chirality-dependent electronic and vibrational shifts of the NTs and of the molecules can be employed to prove the encapsulation, as well as to precisely determine the required encapsulation diameter for the specific molecules under study.

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**CT5**

# Photoconductivity spectroscopy of individual suspended carbon nanotubes

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To investigate photoconductivity of chirality-identified carbon nanotubes, we have fabricated field-effect transistors with individual air-suspended nanotubes [1]. Trenches are etched into $SiO_2$/Si substrates, and Pt/Ti are deposited on both sides of the trenches. By ethanol chemical vapor deposition, carbon nanotubes are grown over the trenches. We have also constructed a system which can simultaneously measure photocurrent and photoluminescence excitation spectra [2]. Nanotubes are excited with a wavelength-tunable continuous wave Ti:sapphire laser, and photoluminescence is detected by an InGaAs photodiode array attached to a spectrometer. Photoluminescence imaging and excitation spectroscopy allows us to locate the nanotubes and identify their chirality. For photocurrent microscopy, excitation laser is modulated by an optical chopper and a lock-in amplifier is used for detection.

Work supported by KAKENHI, The Canon Foundation, The Asahi Glass Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The devices were fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

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**CT6**

# Single chirality desorption of single-wall carbon nanotubes using mixed surfactant gel chromatography

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Previously, we reported a multicolumn gel chromatography method that can separate single chirality single-wall carbon nanotubes (SWCNTs), where a chirality selective adsorption of SWCNT to the gel was utilized [1]. In this study, we have improved the elution process of a single column chromatography and have demonstrated a single chirality separation using chirality selective desorption of SWCNTs.

We used aqueous solution of mixed surfactants, sodium dodecyl sulfate (SDS) and sodium deoxycholate (DOC) for the chirality selective elution. Precisely controlled DOC concentration enabled chirality selective elution and high-purity (6,5) and (7,6) SWCNTs were obtained from a tiny amount of HiPco solution that was not sufficient for the multicolumn method. The chirality distribution of each fraction was analyzed in detail using optical absorption and photoluminescence (PL) spectra. Results suggest the desorption process is highly diameter selective probably due to diameter selective DOC adsorption to SWCNTs. Because this separation is based on a quite simple adsorption chromatography, this method can be easily applicable to a large scale separation of single-chirality SWCNTs.

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**CT7**

# Spontaneous Exciton Dissociation and Stark Effect in Carbon Nanotubes

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Under an application of longitudinal electric fields, we have performed simultaneous photoluminescence and photocurrent measurements on individual single-walled carbon nanotubes. We observe nonzero photoconductivity at small fields, indicating that the injected excitons are spontaneously dissociating into free electron-hole pairs [1]. By modeling the excitation power and voltage dependences of emission intensity and photocurrent, we find that a significant fraction of excitons are dissociating before recombination. We are also able to estimate the absorption cross section and the oscillator strength from the same model. The field-induced redshifts do not depend on excitation power or energy, ruling out effects from heating or relaxation pathways. As the shifts scale quadratically with electric fields, we attribute them to Stark effect [2]. These results show the potential for controlling excitons in individual nanotubes using external electric fields.

Work supported by KAKENHI, SCOPE, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The samples are fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

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**CT8**

# Structure and sorting of DWNTs by diameter and helicity

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Single wall carbon nanotubes (SWCNTs) have shown extrordinary electronic and optical properties since their discovery in 1991 by Iijima et al [1]. However, these properties are highly sensitive to any slight fluctuation in their environment, making their control difficult. On the contrary, double wall nanotubes (DWCNT) offer the advantage that the outer layer can be used as a sacrificial layer, preventing any degradation of the electronic structure of the inner layer [2]. However, interaction between the layers and its impact on their respective properties require to be known in detail.

This is the purpose of the study we have undertaken. DWCNT have been elaborated using CVD techniques [3] In this process, $CH_4$ is thermally decomposed on Co:Mo-MgO catalysts, in order to reach a fraction of DWNTs close to 80%. As a first step, we performed a detailed analysis, by TEM, of the CNT population.

We have found a population of DWNT close to the forcast of 80%. We have observed that nanotubes with an homogeneous diameter distribution, are often grouped into bundles. Statistical analysis of the diameter distribution indicates that diameter of DWNTs down to 1.4 nm can be obtained.

Moreover, thanks to a Cs-corrected JEOL ARM200 operating at 80kV, we have been able to image directly the chiralities of either the intern or the extern wall for different tubes. Numeric FFT of the images have been compared to diffraction simulations using a Fortran code developped by Lambin and Kociak [4]. Results show an excellent agreement between measurements and simulations which confort us in the reliability of this study.

In order to rely diameter distribution, chirality and optical properties, we sorted the primary solution, using the density gradient ultracentrifugation (DGU) and perform optical absorption measurements and TEM for different populations of CNTs. We present our first results on optical and structural characterization of sorted DWCNTs.

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## CT9

# Electron-Phonon Interactions in Ultra Clean Suspended Carbon Nanotubes

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We report pronounced electron-phonon interactions in suspended, nearly defect-free metallic carbon nanotubes, observed through a non-adiabatic Kohn anomaly (KA) of greater strength than theoretically predicted. The phonon energy is studied as a function of Fermi level in the nanotube for the Raman *G*[1] and 2D[2] band. Metallic CNTs have a finite bandgap on the order of the phonon energy (~100meV), which significantly changes the renormalization of phonon energy due to non-adiabatic electron phonon interaction. Using electrical transport measurements, we are able to independently determine this gap, and hence, experimentally demonstrate the effect of this gap on the phonon energy renormalization.

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**CT10**

# Quality Control of Electric Arc Single-Walled Carbon Nanotubes

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Reliable and rapid measurement of the material purity is central to the progress in the bulk production and purification of single-walled carbon nanotube (SWNT) materials. This talk will focus on the application of solution phase near-IR (NIR) spectroscopy for evaluation of carbon nanotube purity, sample preparation and homogenation. Other popular analytical techniques for characterization of SWNT materials, including thermogravimetric analysis (TGA), Raman spectroscopy, SEM and TEM will be discussed. In addition to recent advances in the purification of carbon nanotubes, I will talk about the SWNT thin film technology and its prospects for energy applications and optoelectronic devices.

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## Scope

All kinds of thin-film device applications of nanocarbon materials such as carbon nanotubes and graphenes are included in the scope of this satellite symposium, e.g, (a) active electronic and optical devices such as FETs, TFTs, and optical switches, (b) sensors such as bio sensors, gas sensors, and MEMS/NEMS sensors, (c) passive elements such as transparent conductive films and interconnections, and so on. Fundamental physics and technologies related to those applications such as growth, purification/separation, film formation, printing technology, device fabrication and characterization are also covered.

**K1**

# Monodisperse Carbon Nanomaterial Thin Film Heterostructures

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Improvements in carbon nanomaterial monodispersity have yielded corresponding enhancements in the performance of electronic, optoelectronic, sensing, and energy technologies. However, in all of these cases, carbon nanomaterials are just one of many materials that are employed, suggesting that further device improvements can be achieved by focusing on the integration of disparate nanomaterials into heterostructures with well-defined interfaces. For example, organic self-assembled monolayers on graphene act as effective seeding layers for atomic layer deposited (ALD) dielectrics, resulting in metal-oxide-graphene capacitors with wafer-scale reliability and uniformity comparable to ALD dielectrics on silicon. Similarly, the traditional trade-off between on/off ratio and mobility in semiconducting carbon nanotube (CNT) thin-film transistors (TFTs) is overcome by replacing conventional inorganic gate dielectrics with hybrid organic-inorganic self-assembled nanodielectrics, yielding on/off ratios approaching 106 while concurrently achieving mobilities of ~150 $cm^2$/V-s. Finally, p-type semiconducting CNT thin films are integrated with n-type single-layer $MoS_2$ to form p-n heterojunction diodes. The atomically thin nature of single-layer $MoS_2$ implies that an applied gate bias can electrostatically modulate both sides of the p-n heterojunction concurrently, thereby providing 5 orders of magnitude gate-tunability over the diode rectification ratio in addition to unprecedented anti-ambipolar behavior when operated as a three-terminal device. Overall, this work establishes that carbon nanomaterial thin film applications can be substantially enhanced and diversified into new areas through precise integration into heterostructure devices.

**I1**

# Selective synthesis and extraction of (9,8) single walled carbon nanotubes

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Electronic and optical properties of single-walled carbon nanotubes (SWCNTs) correlate with their chiral structures. Electronic applications need chirally pure SWCNTs while current synthesis methods cannot produce. Here, we show a sulfate-promoted $CoSO_4/SiO_2$ catalyst, which selectively grows large diameter (9, 8) nanotubes at 1.17 nm with 51.7 % abundance among semiconducting tubes, and 33.5% over all tube species. After reduction in $H_2$ at 540 $^{o}$C, the catalyst containing 1 wt% Co has a carbon yield of 3.8 wt%, in which more than 90% is SWCNT. As compared to other Co catalysts used for SWCNT growth, the $CoSO_4/SiO_2$ catalyst is unique with a narrow Co reduction window under $H_2$ centered at 470 °C, which can be attributed to the reduction of highly dispersed $CoSO_4$. X-ray absorption spectroscopy results showed that sulfur content in the catalyst changes after catalyst reduction at different conditions, which correlates with the change in (n, m) selectivity observed. We proposed that the potential roles of sulfur could be limiting the aggregation of Co atoms and/or forming Co–S compounds, which enable the chiral selectivity towards (9, 8) tubes. Further, selective polymer wrapping is a promising approach to further improve the chiral purity of SWCNTs. We showed that among three fluorene-based polymers with different side chain lengths and backbones, poly [(9,9-dihexylfluorenyl-2,7-diyl)-co-(9,10-anthracene)] (PFH-A) can selectively extract SWCNTs synthesized from the $CoSO_4/SiO_2$ catalyst, resulting in enrichment of 78.3% (9,8) and 12.2% (9,7) nanotubes among all semiconducting species. Our results suggest that the matching between the curvature of SWCNTs and the flexibility of polymer side chains and aromatic backbone units is essential in designing novel polymers for selective extraction of (n,m) species.

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**I2**

# Selective Growth of Semiconducting Single-walled Carbon Nanotubes

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Even though the devices made from individual nanotubes have shown outstanding performances such as high mobility, high current, high thermal conductivity, good chemical and mechanical stability, the high hope for the next generation of carbon nanotube based electronics is hampered by several major problems. Among them, is the lack of reliable methods to control the alignment and position of nanotubes as well as, and perhaps most problematically, the growth of nanotubes with controlled chiralities. Even though the post-growth separation of metallic from semiconducting SWNTs have made very good progress, the alignment and assembly of the separated nanotubes into devices are still challenging and not suitable for large scale fabrication. Consequently, a method that can directly produce well aligned arrays of pure semiconducting nanotubes is thought to be the ideal choice for large scale fabrication of nanotubes FETs. In recent years, through systematic studies, we proposed and confirmed a mechanism on the selective growth of semiconducting carbon nanotubes. Important rules were summarized for achieving a high selectivity in growing semiconducting nanotubes by systematically investigating the relationship among water concentration, carbon feeding rate, diameter of catalyst and the percentage of semiconducting nanotubes in the produced SWNT arrays. This understanding will help us to develop better approach to solve the most difficult problem which limited applications of carbon nanotubes in nanoelectronics – the coexistence of metallic and semiconducting nanotubes in samples produced by most, if not all, growth methods.

# I3 Fei Wei

# I4 Andrea Ferrari

# I5 Ali Javey

**I6**

# Light emission and detection with carbon nanotubes

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Carbon nanotubes (CNTs) are direct band gap materials that are not only useful for nanoelectronic applications, but also have the potential to make significant impact on the developments of nanoscale optoelectronic devices. In particular CNTs have been investigated for various electronic and optoelectronic device applications, such as light-emitting diodes[1,2], photodetectors and photovoltaic (PV) cells[3,4]. Semiconducting single-wall CNTs (SWCNTs) are direct-gap materials that can efficiently absorb and emit light. The unique band structure of SWCNT suggests that multiple subbands absorptions can contribute to optoelectric properties. By combining sufficient nanotubes with different diameters, it was also demonstrated that it is possible to gain a nearly continuous absorption response within a broad spectral range (from UV to infrared) to match the solar spectrum [5]. In addition, extremely efficient carrier multiplication (CM) effect has been observed [6], which may potentially lead to a higher energy conversion efficiency than that defined by the Shockley-Quiesser limit. More recently, efficient photovoltage multiplication was also realized via introducing virtual contacts in CNTs, making the output photovoltage of CNT based solar cells a tunable quantity via choosing the diameter of the tube and the number of virtual contacts introduced in the device[7], making it possible for developing optoelectronic communications between nanoelectronic circuits and high performance infrared photodetectors [8-10].

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**I7**

# Stretchable carbon nanotube transistors

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Flexible and stretchable electronics are attracting considerable attention as the next-generation functional electronics because it is believed that in future many electronic assemblies on rigid substrates will be replaced by mechanically flexible or even stretchable alternatives. We have already reported that high density SWCNT film transistors hold carrier mobility of more than 100 $cm^2/Vs$ and on/off ratio of 10,000-100,000 [1]. Based on this method, we fabricated SWCNT transistors on flexible plastic substrates and stretchable poly(dimethylsiloxane) (PDMS) substrates. Particularly, in this study, we improved the fabrication method for stretchable SWCNT. We have preliminary tested expanding durability of devices on PDMS substrates up to strain of 70 % and, during expanding test, both carrier mobility and on/off ratio were approximately constant.

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**I8**

# Aligned Carbon Nanotubes Enabled Functional Thin-film Devices

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Aligned carbon nanotube (CNT) structures possess more efficient transport paths for charges compared with random CNTs. Therefore, high performance optoelectronic devices are expected when the aligned CNT films are used as transparent electrodes. Herein, we report the utilization of the aligned CNT films as window electrodes for CNT–Si heterojunction solar cells and as flexible scaffolds for water-splitting cells and gradient electro-chromic films, respectively. The aligned CNT–Si solar cells show high and stable power conversion efficiency of 10-12%, much higher than that of the devices fabricated using random CNTs. Benefiting from the unique surface of the aligned CNTs, semiconducting oxides such as $TiO_2$ and $WO_3$ are uniformly coated around the CNTs respectively, achieving flexible heterostructure films with interconnected conducting paths inside of the oxide coatings. Such novel structure is highly contrast to the previous CNT-organic hybrids in which CNTs are isolated by the low conductive oxide. The aligned CNT/$TiO_2$ films show an incident photon-to-electron conversion efficiency to be 32% at 320 nm, outperforming $TiO_2$ nanoparticle electrodes for water splitting. The aligned CNT/$WO_3$ films also show greatly improved charge density for proton intercalation. Moreover, due to the anisotropic conducting property of the aligned CNT sheets, the CNT/$WO_3$ films exhibit a very interesting gradient electrochromic phenomenon, with the color changing from yellowish to blue along the nanotube alignment during the coloration.

# I9 Albert Nasibulin

**I10**

# Probing the Chirality-related Information of Single-walled Carbon Nanotubes by Low Voltage SEM

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Chirality controlled growth is a key challenge now in the research field of single-walled carbon nanotube (SWCNT). However, there is still no efficient method for evaluating the chiral indice distribution of as-grown SWCNTs. Here we show that low voltage SEM (LV-SEM) provides a high throughput way for probing the chirality-related information of SWCNTs. For example, metallic and semiconducting SWCNTs display different contrast in LV-SEM. The metallic one shows bright contrast while the semiconducting one shows dark contrast when connected to electrodes. Furthermore, the Schottky barrier at the metal-SWCNT contact can be clearly observed in LV-SEM as a bright contrast segment with length up to micrometers due to the space charge distribution in the depletion region. The lengths of the charge depletion increase with the diameters of semiconducting SWCNTs (s-SWCNTs) when connected to one metal electrode, which enables direct and efficient evaluation of the bandgap distributions of s-SWCNTs. Moreover, this approach can also be applied for a wide variety of semiconducting nanomaterials, adding a new function to conventional SEM.

**CT1**

# Chirality-controlled vapor phase epitaxial growth and termination of carbon nanotubes

Bilu Liu*[1], Jia Liu[1], Chuan Wang[1], Xiaoming Tu[2], Ming Zheng[2], Chongwu Zhou[1]

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Chirality-pure single-wall carbon nanotubes are highly desired for both fundamental study and many of their technological applications. Recently, we have shown that chirality-pure short nanotubes can be used as seeds for vapor-phase epitaxial cloning growth, opening up a new route toward chirality-controlled carbon nanotube synthesis.[1] Nevertheless, the yield of vapor-phase epitaxial growth is rather limited at the present stage, due to the lack of mechanistic understanding of the process. Here we report chirality-dependent growth kinetics and termination mechanism for the vapor-phase epitaxial growth of seven single- chirality nanotubes of (9, 1), (6, 5), (8, 3), (7, 6), (10, 2), (6, 6), and (7, 7), covering near zigzag, medium chiral angle, and near armchair semiconductors, as well as armchair metallic nanotubes. Our results reveal that the growth rates of nanotubes increase with their chiral angles while the active lifetimes of the growth hold opposite trend.[2] Consequently, the chirality distribution of a nanotube ensemble is jointly determined by both growth rates and lifetimes. These results correlate nanotube structures and properties with their growth behaviors and deepen our understanding of chirality-controlled growth of nanotubes.

In the second part, we will briefly report our recent progress on the *in situ* SEM observation of nanotube cloning,[3] and electronic-structure controlled growth of nanotubes from organic chemistry synthesized molecular caps.[4]

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**CT2**

# Robust Transistor of Single Wall Carbon Nanotube in a Network Structure, Rubber Materials and Gel

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Ambient and wearable electronics have received increasing attention for realizing a safe, secure and comfortable smart community, requiring the devices that possess a similar feelings and comparable robustness to clothes. We developed the transistor from all soft organic materials, such as single wall carbon nanotube (SWNT) in a network structure, rubber materials and gel so that all components integrally stretch and absorb applied loadings and impact. The transistor is the side-gated transistor of SWNT channel, ion-gel gate dielectric, and the conductive SWNT rubber electrodes. The transfer characteristic of the side-gated transistor shows that the transistor operates at low voltage and shows high ON/OFF current ratio of 104. We evaluated robustness and stretchability of the transistor systematically by measuring the transistor performance before and after various loadings such as press, bending, stretching and twisting. Our results indicate that the transistor really combines stretchability and robustness comparable to clothes.

**CT3**

# Sub-10 µm top-gate carbon nanotube thin-film transistors based on high-speed flexographic printing process

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Among various thin film transistors (TFTs), carbon nanotube (CNT) TFTs have advantages such as high mobility, flexibility, transparency, printability, and so on. In the previous work, we developed a fully-lithography free and non-vacuum process to fabricate CNT TFTs based on flexographic printing technique, one of high speed printing methods, and achieved a high mobility of 157 $cm^2/Vs$. [1]

In this work, we have improved the resolution of the printing technique for miniaturizing printed CNT TFTs. Flexographic plates were fabricated by using micro-fabrication process. High-purity semiconductor CNTs were used for the channel. Top-gate CNT TFTs with a channel length of ~7 µm was fabricated. The devices showed an on/off ratio of $10^3$ and a mobility of 3.7 $cm^2/Vs$.

This work was partially supported by ALCA-JST, SICORP-JST, and Grant-in-Aid of MEXT.

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**CT4**

# Single-Wall Carbon Nanotube Films Filled with Acceptor Molecules for Transparent Electrodes

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In this work we propose a new approach for modification of optical and electronic properties of thin (thinner than 100 nm) films of single-wall carbon nanotubes (SWNTs) via their gas phase filling with different acceptor molecules (iodine [1], CuCl[2]). The modified films can serve as efficient transparent electrodes with parameters comparable with those of indium tin oxide (ITO) films.

We have realized a gas phase filling of aerosol-grown SWNT films with two types of acceptors – iodine and CuCl. HRTEM measurements have revealed the well-ordered one-dimensional crystals inside nanotubes. With both fillers the optical transparency of SWNT films remained higher than 90%. The optical absorption bands, corresponding to $E_{11}$ transition (for iodine) and both $E_{11}$ and $E_{22}$ transitions (for CuCl) have been suppressed. This happened due to a Fermi level shift into the valence band. The filled SWNT films have demonstrated a drop of electrical resistance of one order of magnitude (down to 70 Ohm/square).

The work was supported by RFBR grants 13-02-01354, 14-02-31818, 14-02-31829, RAS research programs, projects IRSES-295241 and MK-6201.2014.2

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**P1**

# Highly Stable Carbon Nanotube Top-Gate Transistors with Tunable Threshold Voltage

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Carbon nanotubes (SWNTs) are promising materials for electronic applications such as printed circuits, flexible displays and RFID tags. However, the devices general exhibit large hysteresis, uncontrollable polarity and threshold voltages. Here, by utilizing PTrFE as the top gate dielectric, we fabricated hysteresis-free Thin Film Transistors (TFTs) with a threshold voltage around 0 V in ambient conditions. The devices exhibit hysteresis-free operation at different sweep rates at a gate field of 0.5 MV/cm with unipolar device characteristics under both ambient and nitrogen atmospheres. Under a vigorous electrical bias stress test lasting 10000 s, the threshold voltage shifts of our SWNT TFTs are comparable to the recently reported stable organic or metal oxide TFTs. Interestingly, when high-k P(VDF-TrFE-CTFE) was utilized as the top gate dielectric, we also observed a clear ambipolar transistor behavior, even under ambient conditions. Finally, we demonstrate the capability to tune the threshold voltage of both unipolar SWNT TFTs with PTrFE dielectrics and ambipolar SWNT TFTs with P(VDF-TrFE-CTFE) dielectrics by the application of a second gate bias. The ability to tune the threshold voltage of SWNT TFTs in double-gate structures is important for realizing reliable SWNT logic circuits at large scales. [1]

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**P2**

# Carbon Nanotube Thin Film Transistors for Printed Electronics

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We present single-walled carbon-nanotube (SWCNT) thin-film transistors (TFT) fabricated on a plastic substrate using a hybrid manufacturing method. The device structure is a bottom-gate top-contact (BGTC) configuration. The SWCNT networks for the TFT channels were collected onto nitrocellulose membrane filters directly from a floating catalyst-CVD reactor [1]. SWCNT networks were transferred onto plastic PEN substrates, by dissolving the membrane filter by acetone [2]. Before the transfer process, the gate electrodes were shadow-evaporated and polyimide dielectric layer was ink-jet printed on the substrate. The source and drain electrodes were shadow-evaporated on top of the percolating SWCNT network. Finally, another layer of polyimide was ink-jet printed on top of the channel to function as a mask for $O_2$ plasma etching that removed the SWCNTs outside the channel area.

The TFTs were characterized by transfer and output curve measurements using a Keithley 4200 semiconductor characterization system in ambient conditions. The TFTs had parallel plate mobilities on the order of 8 $cm^2/Vs$ and on/off-ratios over $10^5$, with the measurement voltage ranging from -20 V to +20 V. The demonstrated process can be used to fabricate, for example, backplane circuits of flexible displays.

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# GSS14: Fifth Graphene and 2D Materials Satellite Symposium

**Saturday June 7, 2014**
SLH 100
831 Bloom Walk
Los Angeles, CA

**Organizers**
Pertti Hakonen
Jeanie Lau
Katsunori Wakabayashi

## Scope

This Satellite Symposium will focus on fundamental and applied research in the area of graphene and other 2-imensional materials. Graphene is a two dimensional allotrope of carbon, with unique structural and electronic properties. Invited will be presented by leading researchers in the field, to give perspectives on the current status of graphene science and applications. The workshop will consist of both invited and contributed talks spanning these areas. Exchange of results and ideas from different disciplines, and amongst researchers specializing in 2-dimensional materials and/or nanotubes will be highly encouraged.

**Keynote Speakers**
Graphene and Beyond
Antonio Castro Neto (Singapore) keynote 45 min

Transport in graphene heterostructures
Jim Hone (Columbia) keynote 45 min

**Invited Speakers**
Atomically Thin Semiconducting Channels for Future Nano-electronics
Kazuhito Tsukagoshi (NIMS, Tsukuba) 30 min

Two-dimensional Crystals and Nano-scale Devices
Wenjuan Zhu (IBM TJ Watson) 30 min

Thermal transport in graphene and other 2-dimensional materials
Alexander Balandin (UC Riverside) 30 min

Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films
Freddie Withers (University of Manchester) 30 min

Graphene Kirigami
Melina Blees (Cornell) invited 30 min

Graphene Materials for High-Performance Energy Storage
Hui-Ming Cheng (Chinese Academy of Sciences) 30 min

**K1**

# Quantum Transport and Correlated Phenomena in Bilayer and Trilayer Graphene Membranes

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Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a new model system for condensed matter physics, as well as a promising candidate for electronic materials. Though single layer graphene is gapless, bilayer and trilayer graphene have tunable band gaps that may be induced by out-of-plane electric fields or arise from collective excitation of electrons. Here I will present our results on transport measurements in bilayer and trilayer graphene devices with mobility as high as 400,000 cm2/Vs. We demonstrate the presence of an intrinsic gapped state in bilayer and trilayer graphene at the charge neutrality point, stacking-order dependent transport in trilayer graphene, and quantum Hall transitions in these systems. Our results underscore the fascinating many-body physics in these 2D membranes, and have implications for band gap engineering for graphene electronics and optoelectronic applications.

**K2**

# Transport in graphene heterostructures

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To be determined…

**I1**

# Atomically Thin Semiconducting Channels for Future Nano-electronics

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Using atomic-scale thin film of metal chalcogenide layered material, we have developed semiconducting channel for future electronics. We investigated transport properties, particularly scattering property of carrier transport. In this transport experiment, it is found that the carrier scattering from interfacial Coulomb impurities is greatly intensified in extremely thinned channels, resulting from shortened interaction distance between impurities and carriers.

Thus, we fabricated $MoS_2$ field-effect transistors on crystalline hexagonal boron nitride (h-BN) and $SiO_2$ substrates. Temperature dependence of these transistors shows distinct weak temperature dependence of the $MoS_2$ devices on h-BN substrate. At the room temperature, mobility enhancement and reduced interface trap density of the single and bilayer $MoS_2$ devices on h-BN substrate further indicate that reducing substrate traps is crucial for enhancing the mobility in atomically thin $MoS_2$ devices. More detail of carrier scattering in the atomic-scale thin channel will be discussed.

Furthermore, we have developed field effect transistor using high-k flak dielectric with layered structure.

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**I2**

# Two-dimensional Crystals and Nano-scale Devices

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In the last few years, the research community has seen rapidly growing interest in two-dimensional (2D) crystals and their applications. The electronic properties of these 2D crystals are diverse — ranging from semi-metals, such as graphene, to semiconductors, such as $MoS_2$, to insulators, such as boron nitride. These 2D crystals have many unique properties as compared to their bulk counterparts due to their reduced dimensionality and symmetry. A key difference is the band structures, which lead to distinct electronic and photonic properties. The 2D nature of the materials also plays an important role in defining their exceptional properties of mechanical strength, surface sensitivity, thermal conductivity, tunable band-gap and interaction with light. These unique properties of 2D crystals open up broad territories of applications in computing, communication, energy, and medicine. In this talk, I will present our work on understanding the electrical properties of graphene and $MoS_2$, in particular current transport and band-gap engineering in graphene, interface between gate dielectrics and graphene, and gap states in $MoS_2$. I will also present our work on the nano-scale electronic devices (RF and logic devices) and photonic devices (plasmonic devices and photo-detectors) based on these 2D crystals.

**I3**

# Thermal transport in graphene and other 2-dimensional materials

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Phonons reveal themselves in all electrical and thermal phenomena in materials. Acoustic phonons carry heat and limit electron mobility. Nanostructures open opportunities for tuning the phonon spectrum and related properties of materials for specific applications, thus realizing what was termed phonon engineering [1]. A recent advent of graphene and other two-dimensional materials resulted in a discovery of a wealth of new phonon physics and created opportunities for better control of phonon transport. In this talk, I will describe the measurements of the phonon thermal conductivity of graphene using the optothermal Raman technique [2-3]; explain physical phenomena leading to the anomalous behavior of the thermal conductivity of graphene [3-4]; and outline practical applications of graphene in thermal management of electronics [5-6]. The unique phonon properties of a broad class of two-dimensional materials will also be discussed. Specifically, I will address increasing thermoelectric figure of merit in stacks of layered materials [7], the use of Raman spectroscopy as nanometrology tool for quasi 2D crystals [8], and modification of the transition temperature to the charge-density-wave phase in two-dimensional films of van der Waals materials [9].

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**I4**

# Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films

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The arrival of graphene and other layered materials has led to the production of novel hetero structures. Such structures show great promise for future flexible and semi transparent devices. These heterostructures are currently produced by mechanically exfoliating single or few layers of different crystals and combining them to construct vertical electronic and optoelectronic devices. One such device is the vertical transistor, where single layer graphene flakes sandwich a semiconducting tunnel barrier. In these devices the vertical tunnel current can be tuned by means of a back gate. In the case of a h-BN tunnel barrier the vertical tunnel current can only be tuned weakly due to the large band gap of the h-BN. However when the band gap of the tunnel barrier is reduced the vertical tunnelling current can be tuned by over 4 orders of magnitude. Suitable barrier materials are the transition metal dichalcogenides (TMDC's) such as $MoS_2$ or $WS_2$. The band gap of few layer TMDC materials is smaller (~ 1.5 eV) than optical energies. This means that when excited with optical irradiation a significant number of electron hole pairs are generated. If the sandwiching graphene flakes are asymmetrically doped then the in-built electric field separates carriers and a significant photocurrent is observed. External quantum of efficiencies of ~ 30 % have been obtained.

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**I5**

# Graphene Kirigami

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We apply the principle of kirigami, a paper art that includes cutting, to monolayer graphene to create moving parts at the nanoscale. We begin by lifting patterned graphene devices off a surface into liquid, where we can fold the atom-thick sheet like paper. We create simple cantilever devices to measure the out-of-plane bending stiffness of graphene, a key material property. We find that the stiffness is significantly higher than simple theories predict, but is well explained by membrane fluctuation theory. We then take advantage of graphene's extraordinary mechanical properties to create resilient, atomically thin hinges and three-dimensional structures. Selective cuts create in-plane and out-of-plane springs with pattern-dependent spring constants, turning graphene into a mechanical metamaterial. Finally, we show that we can actuate these devices remotely using lasers and magnetic fields. This simple but powerful technique for altering graphene's mechanical response promises resilient, customizable moving parts at the nanoscale.

**I6**

# Graphene Materials for High-Performance Energy Storage

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Graphene has many excellent properties, such as high specific surface area, good chemical stability, high electrical and thermal conductivity, high mechanical properties, and excellent flexibility. So graphene and its composite materials are expected to be used in high-performance energy storage devices. Synergistic effects between graphene and electrode materials and the beneficial roles of graphene in composite electrodes are widely found. It is demonstrated that, when the composites are used as electrode materials for lithium storage, compared to their individual constituents, graphene composites with unique structures such as anchoring, wrapping, encapsulating, sandwiching, buffering, layering and mixing have a significant improvement in their electrochemical properties such as high capacity, high rate capability and excellent cycling stability. The roles of graphene are considered to form a conductive network, increase electron and lithium ion conductivity, and anchor and trap electrode materials, and their efficiency is dependent upon how strong the interaction between graphene and electrode materials is.

Graphene can also be used in flexible batteries and Li-S batteries. By coating active materials on a three-dimensional interconnected graphene framework (GF) developed at our lab, an anode and cathode were made to assemble a thin, lightweight and flexible lithium ion battery. The battery has shown high rate capability and capacity, and can be repeatedly bent down to <5 mm without failure and degradation of its electrochemical performance. We also designed a unique sandwich structure with pure sulfur between two graphene membranes for a Li-S battery to trap polysulfides. One graphene membrane was used as a current collector with sulfur coated on it as the active material, and the other graphene membrane was coated on a commercial polymer separator. The battery shows significant improvement in cyclability and capacity, because the electrode with two graphene membranes can provide rapid ion- and electron transport paths, accommodate sulfur volumetric expansion and store and reuse migrating polysulfides to alleviate the shuttling effect. The fabrication of large-scale graphene materials has already been demonstrated, therefore, it is not too far from graphene materials to be used commercially for high-efficiency energy storage.

**CT1**

# Substrate–graphene interactions and lowering of graphene symmetry in CVD growth

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In the chemical vapor deposition (CVD) synthesis of graphene, the role of the substrate is often viewed as relatively "passive", facilitating the decomposition of precursor gas into carbon atoms and providing planar template for these atoms to assemble into the graphene layer, guided by their own covalent interactions. In this framework it is possible to construct useful models of graphene growth that can explain/predict the morphology of graphene islands under thermodynamic and kinetic control. Our "nanoreactor" model [1] accounts for a diversity of experimentally observed graphene shapes including zigzag-edged hexagons, dodecagons with six zigzag and six armchair edges, and even unusual lowered-symmetry dodecagons with non–30-degree angles, all determined by the anisotropies of graphene's edge energy and growth speed. Here we extend the previous theory to add the substrate into the picture, showing how the interaction of graphene with the substrate affects the edge energy and growth speed bringing about thermodynamically and kinetically controlled crystal shapes that do not share the full symmetry of graphene lattice. Through a detailed first-principles analysis and coarse-grained Monte Carlo growth simulations we are able to explain a large diversity of experimentally observed low-symmetry shapes of graphene such as triangles or distorted hexagons, frequently observed in graphene CVD growth on Ni and Cu substrates, as well as for other materials such as BN or metal dichalcogenides.

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**CT2**

# Defect-engineered Group IV Surfaces for Phononic Circuits

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Phononics or phonon engineering involves the control and manipulation of phonons. With the increasing focus on design and development of non-charge based devices, phononic computing is emerging as an alternative computing paradigm to the conventional electronic and optical computing, increasing our ability to manipulate and store information in the nanoscale. To realize these phononic devices within existing conventional architectures, phononic components such as waveguides, resonators, and switches are needed.

In this study, we propose and analyze various phononic circuit building blocks, such as nano-scaled phononic resonators, waveguides and switches, realized on <111> surfaces of group IV elements, such as 3C-SiC and 3C-GeSi. This is achieved by simultaneously introducing defects of various types, and by varying their specific locations on the surface. To calculate the defect-induced vibrational properties, such as the phononic bandgap, the total phonon density of states, and the partial phonon density of states, we used molecular dynamics with semi-empirical potentials. Manipulating phononic properties with defect engineering could provide a new route towards designing building blocks of phononic circuits operating at THz frequencies.

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CT3

# Exfoliated Few-Layered $WSe_2$ Phototransistors

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We report on the fabrication of phototransistors based on exfoliated flakes of $WSe_2$ with few atomic layer thicknesses. Chemical vapor transport grown $WSe_2$ crystals were mechanically exfoliated and transferred to Si substrates with a top $SiO_2$ layer (285 nm thick). Electron beam lithography was used to create electrical contacts on the $WSe_2$ semiconducting flakes; these contacts act as source and drain terminals of the field effect transistor, meanwhile the heavily doped silicon body was connected and used as gate. The morphology and chemical composition of the flakes were determined by an extensive characterization by Raman and atomic force microscopy. The photocurrent generation on these phototransistors was characterized under two illumination conditions, first under the focused beam of the confocal Raman spectrometer and also under flooded illumination using either room light or monochromated light. The resulting photoresponse reveals dependence on the illumination wavelength and also on the applied gate voltage, besides the well-known dependence on the drain source potential. It was found that $WSe_2$ phototransistors have excellent electrical characteristics possible produced by the relatively high carrier mobility. The devices tested here reached photoresponse in the range of few A/W and fast response times in the micro second range. $WSe_2$ is a TMD material with great potential for optoelectronics application because the band gap is ~1.65 eV which makes it sensitive to the whole visible spectrum.

CT4

# Graphene Nucleation on a Surface-Molten Copper Catalyst: Quantum Chemical Molecular Dynamics Simulations

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Chemical vapordeposition (CVD) graphenegrowth on Cu(111) hasbeenmodeled with quantum chemicalmolecular dynamics (QM/MD) simulations. These simulations demonstrate at the atomic levelhow graphene forms on Cu surfaces. In contrast to other popular catalysts, such as nickel and iron, copper is in a surface molten state throughout graphene growth at CVD-relevant temperatures, and graphene growth takes place without subsurface diffusion of carbon. Surface Cu atoms have remarkably high mobility on the Cu(111) surface, both before and after graphene nucleation. This surface mobility drives “defect healing” processes in the nucleating graphene structure that convert defects such as pentagons and heptagons into carbon hexagons. Consequently, the graphene defects that become “kinetically trapped” using other catalysts, such as Ni and Fe, are less commonly observed in the case of Cu. We propose this mechanism to be the basis of copper’s ability to form high-quality, large-domain graphene flakes.

**CT5**

# Ultrafast quantitative nanomechanical mapping of suspended graphene

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I present quantitative nanomechanical maps of suspended graphene membranes, both monolayer and multilayer. Peakforce QNM, a new off resonance tapping AFM mode, allows rapid mapping of force response curves at every pixel, two orders of magnitude faster than conventional force volume mapping. A range of nanomechanical properties, including the adhesion, modulus, dissipation and deformation can then be extracted in real time along with the topographic data. Circular holes were created in silicon nitride membranes on silicon supports via a SF6 etch using a photolithographically defined etch mask. Mechanically exfoliated graphene flakes were then transferred onto the nitride membrane, leaving an array of suspended circular areas suitable for transmission characterization methods as TEM as well as AFM. The adhesion of the flakes to the silicon nitride membrane was also investigated, and compared with previously published results on silicon dioxide substrates.

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**CT6**

# Theoretical Limits to Suspended Graphene Varactors and Tunneling Relays

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The high yield strength, low flexural rigidity and low mass density of suspended graphene membranes are potentially promising for nanoelectromechanics applications. We have explored the theoretical limits to graphene varactor and tunneling relay performance. The suspended graphene varactor, where capacitance is tuned by electrostatic actuation of membrane deflection, provides a capacitor tuning range of ~76%, with a membrane pull-in voltage $V_p$ as low as ~1V. An intrinsic electrical quality factor as high as 200 is predicted at 1 GHz for these devices [M. AbdelGhany et al. Appl. Phys. Lett. 101, 153102 (2012).]. Nonlinear currents arising from capacitance modulation under sinusoidal drive are predicted to appear at odd harmonics, with amplitude proportional to $(V_{ac}/V_p)^{5/3}$. We have also considered the theory of the tunneling relay, where the electrostatic actuation of a graphene membrane is combined with the exponential dependence of tunneling current through a vacuum gap. Sub-threshold swings as steep as 10 mV/decade are predicted, breaking the thermionic limit of 60mV/decade at room temperature [M. AbdelGhany et al. Appl. Phys. Lett. 104, 013509 (2014).]. The predicted performance suggests that a significant reduction in dynamic energy consumption over conventional field effect transistors is physically achievable. We will report on our recent experimental progress towards realizing graphene nanoelectromechanical devices with large area graphene.

CT7

# Silicon-carbon bond inversions driven by 60 keV electrons in graphene

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Single-layer graphene is arguably an ideal material for atomic resolution electron microscopy. But even in the so-called 'gentle' conditions used for atom-by-atom investigations, beam damage effects cannot be neglected. Imperfections such as doping also change the effect an electron beam has on the atomic structure of graphene, as we have recently shown for nitrogen substitutions [1].

We now demonstrate that 60 keV electron irradiation drives the diffusion of threefold coordinated Si dopants in graphene by one lattice site at a time [2]. First principles molecular dynamics simulations reveal that each step is caused by an electron impact on a C atom next to the dopant. Although the atomic motion happens below our experimental time resolution, stochastic analysis of 38 such lattice jumps reveals a probability for their occurrence in a good agreement with the simulations.

Conversions from three- to fourfold coordinated dopant structures and the subsequent reverse process are significantly less likely than the direct bond inversion. Our results thus provide a model of non-destructive and atomically precise structural modification and detection for two-dimensional materials.

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**CT8**

# Large Area Graphene Ion Sensitive Field Effect Transistors with Tantalum Pentoxide Sensing Layers for pH Measurement

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We have fabricated and characterized large area graphene ion sensitive field effect transistors (ISFETs) using different pH buffer solutions. We use resistive and capacitive measurement of graphene's Fermi level versus changes in pH. Bare graphene devices are insensitive to changes in pH due to the absence of surface sites available to participate in the protonation and deprotonation process necessary for pH sensing. Deposition of a thin layer of $Ta_2O_5$ by atomic layer deposition increases the density of surface sites, enhancing the buffering capacity of the sensing surface layer, thus increasing the sensitivity of graphene based ISFETs. We have achieved a linear pH sensitivity up to 32.5 mV/pH and we interpret our results using the Bergveld ISFET model. Device response is stable over ~ two weeks. We will report our recent work towards reaching the Nernstian limit of 60 mV/pH sensitivity.

CT9

# Study of ammonia absorption on reduced graphene fluoride

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Since the discovery of graphene, many investigations have focused on the study of unique properties of this material. It has been shown that the interaction between a graphene surface with polar molecules in a gas phase leads to a change in its electronic state [1]. With adsorption of polar molecules on the surface, the charge transfer occurs from the molecules to the graphene plane [2]. To enhance the sensing properties, we create reactive centers on the surface by functionalizing graphene layers with fluorine.

The aim of this work is to study the structural and electrical properties of partially reduced graphene fluoride as well as to determine the effect of the reduction degree on the response induced by adsorbed molecules of ammonia. Using our proposed recovery technique [3], the samples were obtained with different degrees of reduction and exposed to gas mixtures with different contents of ammonia. The response amplitude, response and recovery times depend on the reduction degree. Moreover, the equilibrium adsorption /desorption constants and adsorption heat were evaluated using the Langmuir equation. The experimental data are in correlation with the numerical simulations of the interaction of a fluorographene fragment with ammonia molecules.

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