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NSS8
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28-31 july 2014

Nanoscale Spectroscopy and Nanotechnology 8

Scientific Program

Gleacher Center
Chicago, USA

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SPECS™

NSS 8 Scientific Program
Monday (28 July 2014)

7:30-8:15	**Registration** (6th floor, Gleacher Center)

8:15-8:30	**Welcome Statement**
8:30-9:15 **Plenary**	*Session Chair:* ***A. Hoffmann*** *(ANL)* Complex spin states revealed and locally manipulated by 3D-vector resolved spin-polarized tunneling techniques **R. Wiesendanger** (*Univ. Hamburg, Germany*).
9:15-9:30	**Break**
9:30-10:06	*Session Chair:* ***Y. Kim*** *(RIKEN)* (**Invited**) Nanowires as a generic technology for science and applications **L. Samuelson**. *Lund University, Solid State Physics & Nanometer Structure Consortium, and ,QuNano AB, Glo AB & Sol Voltaics AB, Ideon Science Park, Lund, Sweden.*
10:06-10:42	(**Invited**) Electronic structure and exciton formation at ZnO interfaces **M. Wolf**. *Department of Physical Chemistry, Fritz-Haber-Institute, Berlin, Germany.*
10:42-11:00	**Break**

	(Room A) 2-D Nanostructures *Session Chair:* ***J.W.M. Frenken*** *(Leiden Univ., Netherlands)*	**(Room B) Synchrotron SPM** *Session Chair:* ***D. Tonneau*** *(Marseille, France)*
11:00-11:18	(**Invited**) Functional nanomaterial heterostructures **M. C. Hersam**. *Materials Science and Engineering Dept., Northwestern University, USA.*	(**Invited**) Pico-imaging by X-ray-nnduced effects using SR-based STM. **A. Saito**, Y.Furudate, Y.Kusui, T.Saito, M.Akai-Kasaya, Y.Tanaka, K.Tamasaku, Y.Kohmura, T.Ishikawa, Y.Kuwahara and M.Aono. *Dept. Precision Sci.& Technol.,Graduate School of Engineering, Osaka Univ., RIKEN SPring-8 Center, Sayo-cho, Hyogo, National Inst. for Materials Science, Tsukuba, Ibaraki, Japan*
11:18-11:36	Invited talk continued.	Invited talk continued.
11:36-11:54	Three dimensional graphene-gold nanoparticles hybrid structure for surface enhanced raman spectroscopy. **J. Leem**, M. C. Wang, S. W. Nam *Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, USA.*	Low temperature synchrotron X-ray scanning tunneling microscopy (LT-SXSTM). **N. Shirato**, H. Kersell, C. Preissner, S.-W. Hla, V. Rose.*X-ray Science Division, Argonne National Laboratory,Department of Physics and Astronomy, Ohio University, Center for Nanoscale Materials, Argonne National Laboratory, USA.*
11:54-12:12	Three-dimensional Textured Graphene Bioelectronics. M.C. Wang, S.G. Chun, **S.W. Nam** *Mechanical Science and Engineering, Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, USA.*	Synchrotron X-ray scanning tunneling microscopy (SXSTM) at the Advanced Photon Source. **M. Cummings**, N. Shirato, B. Stripe, C. Preissner, D. Rosenmann, S.-W. Hla, V. Rose. *Advanced Photon Source, and Center for Nanoscale Materials, Argonne National Laboratory, USA.*
12:12-14:30	**Lunch Break**	**Lunch Break**

	(Room A) Nanobio *Session Chair:* ***J.M. Cole*** *(Univ. of Cambridge, UK)*	**(Room B) Synchrotron SPM** *Session Chair:* ***A. Saito*** *(Osaka, Japan)*
14:30-14:48	(**Invited**) TiO_2 biocomposites within cell machiner. T. Koritarov, V. Konda, R. Mustafi, M. Bissonnett, **T. Rajh**. *Center for Nanoscale Materials, Argonne National Laboratory, Department of Medicine, The University of Chicago USA.*	(**Invited**) Nanometer scale resolution topography combined to local photon spectroscopy. C. Fauquet, H. Maradj, M. Dehlinger, A. Erko, A. Bjeoumikhov, **D. Tonneau.** *Aix-Marseille Univ., and CNRS-UMR7325, Marseille, France, Institute for Nanometre Optics and Technology, Helmholtz-Zentrum Berlin, Germany, and IFG-GmbH, Berlin, Germany.*
14:48-15:06	Invited talk continued.	
15:06-15:24	The correlation between cytoskeletal structure and cell mechanics in human pulmonary artery endothelial cells. **X. Wang**, M. E. Brown, R. Bleher, S. Dudek, G. S. Shekhawat, V.P. Dravid. *Dept. of Materials Science and Engineering, Northwestern University, and Dept. of Medicine, University of Illinois, Chicago, USA.*	Fabrication and characterization of smart CNT-based tips for synchrotron assisted STM. **H. Yan**, M. Cummings, F. Camilo, D. Rosenmann, M. Lu, X. Tong, W. Xu, V. Rose, E. Nazareski. *Brookhaven National Laboratory, NY, Argonne National Laboratory, Argonne, IL, and CFN, Brookhaven National Laboratory, NY, USA.*
15:24-15:42	Bacteria at the nanoscale – bacterial stress response investigated by X-ray fluorescence and X-ray microscopy. **R. Heine**, Y. Yang, S. Kirchen, R. Debastiani, T. Gorniak, T. Senkbeil, A. Rosenhahn, F. Xu, H. Suhonen, L. Helfen, C. Bartels, I. Wacker, Y.F. Song,C.C. Wang, B. Stripe, V. Rose, M. Grunze, T. Schwartz, T. Baumbach. *ANKA/IPS, and IFG Karlsruhe Institute of Technology, Germany. Analytical Chemistry - Biointerfaces, Ruhr-University Bochum, Germany. ESRF, Grenoble, France, CryoEM, Center for Advanced Materials, Heidelberg, Germany, NSRRC – Hsinchu, Taiwan, Argonne National Laboratory, USA, and APC, University of Heidelberg, Germany.*	Smart MIM Tips for Next-Generation X-ray Scanning Tunneling Microscopes. **D. Rosenmann**, M. Cummings, N. Shirato, D. Miller, R. Winarski, S-W. Hla, V. Rose, *Center for Nanoscale Materials, Argonne National Laboratory, Advanced Photon Source, Argonne National Laboratory, Electron Microscopy Center, Argonne National Laboratory, and Ohio University, Physics and Astronomy Department, USA.*
15:42-16:00	**Break**	**Break**

	(Room A) TEM *Session Chair:* ***L. Samuelson*** *(Lund, Sweden)*	**(Room B) Synchrotron Applications** *Session Chair:* ***Y. Takahashi*** *(Hyogo, Japan)*
16:00-16:18	(**Invited**) SiC nanowires: a cytocompatible tool for nanomedicine. **G. Salviati**. *IMEM-CNR, Parco Area delle Scienze 37/A, 43124 Parma, Italy*	(**Invited**) Exploring ZnO nanostructures by synchrotron-based scanning x-ray and photoelectron microscopes. **M. K. Abyaneh**, B. Bozzini, T. Araki, B. Kaulich *Diamond Light Source Ltd., UK, and Dipartimento di Ingegneria dell'Innovazione, Univ. del Salento, Lecce, Italy.*
16:18-16:36	Invited talk continued.	Invited talk continued.
16:36-16:54	Visible luminescence of sulfur-doped micro-structured black silicon analyzed at the nanoscale. **F. Fabbri**, Y.-T. Lin, M. J. Smith, E. Mazur, S. Gradecak, G. Salviati. *IMEM-CNR Institute, Parco Area delle Scienze, Parma, Italy, School of Engineering and Applied Sciences, Harvard University, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, and Dept. of Physics, Harvard Univ., USA.*	(**Invited**) Nanotomographic imaging techniques at the hard X-ray nanoprobe. **R. P. Winarski** *Nanoscience and Technology Division, Argonne National Laboratory, USA.*
16:54-17:12	Electron microscopy evidences on relevance of microstructure - property correlations. **A. K. Srivastava.** *National Physical Laboratory, Council of Scientific and Industrial Research*, *New Delhi, India.*	Invited talk continued.
17:12-17:30		Nanoscale computed tomography reconstructions with overlaid 3D quantized fluorescence. **B. Stripe**, R. Winarski, L. Trahey, D. Rosenman, R. Divan, V. Rose. *Advanced Photon Source, Center for Nanoscale Materials, and Chemical Sciences and Engineering, Argonne National Lab, USA.*

17:30-18:30	***Poster Session*** *(6th Floor)*

Tuesday (29 July 2014)

8:30-9:15 **Plenary**	*Session Chair:* ***V. Rose*** *(ANL)* Nanoscale studies of a 19th century daguerreotype photograph **E.P. Vicenzi** (*Museum Conservation Institute, Smithsonian Institution, USA)*.
9:15-9:30	**Break**
9:30-10:06	*Session Chair:* ***A.R. Smith*** *(Ohio Univ.)* (**Invited**) Connecting spin waves to charge currents. **A. Hoffmann**. *Materials Science Division, Argonne National Laboratory, USA.*
10:06-10:42	(**Invited**) Supramolecular architectures at surfaces for probing structure, electron and spin states. N. Ballav, M. Stöhr, J. Lobo-Checa, P. M. Oppeneer, L.H. Gade, S.Decurtins, F.Diederich, C.Thilgen, A. Kleibert, **T. A. Jung** *Dept. of Synchrotron Radiation, Paul Scherrer Institute, Switzerland, Dept. of Physics, University of Basel, Switzerland, Dept. of Physics and Astronomy, Uppsala University, Sweden, University of Heidelberg, Germany, Dept. of Chemistry, ETH Zürich, Switzerland, Univ. of Bern, Switzerland, Zernike Institute for Advanced Materials, University of Groningen, Netherlands, and Centro de Física de Materiales (CSIC-UPV/EHU),San Sebastián, Spain.*
10:42-11:00	**Break**

	(Room A) 2-D Nanostructures *Session Chair:* ***S. Heun*** *(Pisa, Italy)*	**(Room B) Nanofabrication** *Session Chair:* ***D. Lopez*** *(CNM-ANL)*
11:00-11:18	(**Invited**) Live STM observation of the growth of graphene and *h*-BN. **J.W.M. Frenken**, D.W. van Baarle, G.Dong. *Advanced Research Center for Nano-Lithography, Amsterdam, and Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands*	(**Invited**) Nanofabrication of diffractive X-ray optics for applications at synchrotrons and XFELs. **C. David**, P. Karvinen, I. Vartiainen, I. Mohacsi. *Paul Scherrer Institut, Switzerland*.
11:18-11:36	Invited talk continued.	Invited talk continued.
11:36-11:54	Solid-source growth and atomic scale characterization of graphene on Ag(111). B. Kiraly, A. Mannix, M. Hersam, **N. Guisinger**. *Northwestern University, and Argonne National Laboratory, USA.*	3D electron beam lithography for bio-medical applications. K. Maamari, K. Punchihewa, E. Zaker, D. Datta, R. Nathani, F. Mazza, M. Mengoni, V. Metlushko *Dept. of Electrical and Computer Engineering, Univ. of Illinois at Chicago, USA.*
11:54-12:12	Silicon growth at the two-dimensional limit on Ag(111). **A. Mannix**, B. Kiraly, B. Fisher, M. Hersam, N. Guisinger. *Center for Nanoscale Materials, Argonne National Laboratory, Dept. of Materials Science and Engineering, Northwestern University, and Dept. of Chemistry, Northwestern University, USA.*	Heteroepitaxial growth of organic superconductors on Ag(111). E. Zupanic, Z. Biao, A. Miyazaki, M. Tokumoto, I. Musevic, H. Kobayashi, A. Kobayashi, **A. Hassanien.** *Jozef Stefan Institute, Ljubljana, Slovenia, Nihon University, Tokyo, Toyama University, Toyama, and AIST, Tsukuba, Japan.*
12:12-14:30	**Lunch Break**	**Lunch Break**

	(Room A) Solar/Molecular Processes *Session Chair:* ***T. Rajh*** *(CNM-ANL)*	**(Room B) Molecular Machines** *Session Chair:* ***M. Wolf*** *(FHI Berlin, Germany)*
14:30-14:48	Decoding the mystery of additives in organic solar cells. W. Chen, **S.B. Darling**. *Materials Science Division, and Center for Nanoscale Materials, Argonne National Laboratory, and Institute for Molecular Engineering, University of Chicago, USA.*	(**Invited**) Solar-powered molecular transducers: Towards energy sustainable nanomachines. **J. M. Cole**. *Cavendish Laboratory, University of Cambridge, UK.*
14:48-15:06	Fast optoelectronic spectroscopy of a cuprous oxide/copper schottky barrier photovoltaic device. **L. Frazer**, K. B. Chang, L. Ocola, L. Stan, D. Rosenmann, K.R. Poeppelmeier, J, B. Ketterson. *Dept. of Physics and Astronomy, Dept. of Chemistry, and Dept. of Electrical Engineering and Computer Science, Northwestern University, Center for Nanoscal Materials, Chemical Sciences and Engineering Division, Argonne National Laboratory, USA.*	Invited talk continued.
15:06-15:24	Layer-by-layer fabrication of oriented porous thin films based on porphyrin-containing metal-organic framework. **Monica C. So**, S. Jin, H.-J. Son, G.P. Wiederrecht, O.K. Farha, J.T. Hupp. *Dept. of Chemistry, Northwestern University, and Nanoscience & Technology Division, Argonne National Laboratory, USA.*	Entangled and synchronized rotation of molecular machines **H. Kersell**, V. Iancu, Y. Zhang, R. Stefak, G. Rapenne, S. W. Hla. *Nanoscale and Quantum Phenomena Institute, Ohio Univ., USA,CEMES, CNRS, and Université de Paul Sabatier, Toulouse, France, Center for Nanoscale Materials, Argonne National Laboratory, USA.*
15:24-15:42	Thickness dependence of electronic structures of single H_2Pc on NaCl ultrathin insulating films. **M. Imai**, H. Imada, T. K. Shimizu, M. Kawai, Y. Kim. *Dept. of Advanced Materials Science, the University of Tokyo, Surface and Interface Science Laboratory, RIKEN, and National Institute for Materials Science, Tsukuba,Japan.*	Controlled rotation and manipulation of individual molecular motors. **Y. Zhang**, U.G.E. Perera, F. Ample, H. Kersell, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, C. Joachim, S.-W. Hla. *Ohio Univ.,USA, CEMES, CNRS, Toulouse, and Université de Paul Sabatier, Toulouse, France, and IMRE, A*STAR, Singapore.*
15:42-16:00	**Break**	**Break**

	(Room A) Nanoparticles *Session Chair:* ***C. David*** *(PSI, Switzerland)*	**(Room B)** *Session Chair:* ***S. Foelsch*** *(PDI, Germany)*
16:00-16:18	(**Invited**) Coherent diffraction imaging with focused hard X-ray beams. **Y. Takahashi**.*Graduate School of Engineering, Osaka University, Osaka, and RIKEN SPring-8 Center, Hyogo, Japan.*	(**Invited**) Self-assembled donor-acceptor hetero-junctions at the atomic scale: chirality, charge transfer and reversible rectification. J.A. Smerdon, R.B.Rankin, N.C. Giebink, J. Cho, L. Gao, O. Suzer, J. P. Greeley, N. P. Guisinger, **J. R. Guest**.*Univ. of Central Lancashire, UK, Villanova Univ., Penn State University, California Institute of Technology, and California State University, Northridge, HGST, San Jose, Purdue University, and Argonne National Laboratory, USA.*
16:18-16:36	Invited talk continued.	Invited talk continued.
16:36-16:54	Wide area distribution of homogeneous nanoparticles using inert gas condensation process. **S.G. Pandya**, M. E. Kordesch. *Ohio University, USA.*	Formation and hydrogenation of atomic nitrogen on Pt(111). **Z. Liang**, H.J. Yang, J. Oh, Y. Kim, M. Trenary. *Dept. of Chemistry, University of Illinois at Chicago, USA, and Surface and Interface Science Laboratory, RIKEN, Japan.*
16:54-17:12	Free-standing nanoparticle monolayers. **E. Barry**, S.P. McBride, H.M. Jaeger, X.-M. Lin. *Argonne National Laboratory, and James Franck Institute, University of Chicago, USA.*	(**Invited**) Tracking vacancies through imaging, spectroscopy and first-principles theory. **S. J. Pennycook**, J. Gazquez, N. Biškup, J. Salafranca, C. Cantoni, M. Varela, S.T. Pantelides· *Dept. of Materials Science and Engineering, University of Tennessee, Materials Science and Technology Division, Oak Ridge National Laboratory, USA, Dept. de Física Aplicada III, Universidad Complutense de Madrid, Spain, Dept. of Physics and Astronomy, Vanderbilt University, USA.*
17:12-17:30	Fine structure splitting and electric field confinement effects of quantum dot molecules. **R. Thota**, S. Ramanathan, G. Petersen, K. Wijesundara, M. Kerfoot, M. Schiebner, A.S. Bracker, D. Gammon, E. Stinaff. *Nanoscale and Quantum Phenomena Institute, Ohio University,University of California, Merced, and Naval Research Labs, Washington DC, USA.*	Invited talk continued.

17:30-18:30	***Poster Session*** *(6th Floor)*

Wednesday (30 July 2014)

8:30-9:15 **Plenary**	*Session Chair:* ***N. Yamamoto*** *(TIT, Tokyo, Japan)* Single molecule spectroscopy using STM **M. Kawai** (*University of Tokyo, Japan*).
9:15-9:30	**Break**

	(Room A) STM Manipulation *Session Chair:* ***K. Franke*** *(Free Univ., Germany)*	**(Room B) 2-D Nanostructures** *Session Chair:* ***H. Shigekawa*** *(Tuskuba, Japan)*
9:30-10:06	(**Invited**) Assembling and probing quantum structures on a semiconductor surface by cryogenic STM. **S. Fölsch**. *Paul Drude Institute for Solid State Electronics, Berlin, Germany*	(**Invited**) Scanning tunneling microscopy and spectroscopy studies of graphene in the quantum hall regime. **A. Luican-Mayer**, E.Y. Andrei, S. W. Hla. *Center for Nanoscale Materials, Argonne National Laboratory, and Dept. of Physics and Astronomy, Rutgers University, USA.*
10:06-10:24	Joule-Thomson scanning probe microscope for in-situ analysis in extreme environments. **V. Simic-Milosevic**. *SPECS Surface Nano Analysis GmbH, Berlin, Germany.*	Graphene silicon interfaces at the two-dimensional limit. **B. Kiraly**, A. Mannix, M. Hersam, N. Guisinger. *Northwestern University, and [2]Argonne National Laboratory, USA.*
10:24-10:42	Manipulating charge states of metal-semiconductor interfaces. **T.-H. Kim**, H.W. Yeom. *Dept. of Physics, Pohang University of Science and Technology, and Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science, Pohang, Republic of Korea*	Modeling of photo-induced transport in two-dimensional semiconductors. **E.J. Lenferink**, Y. Jia, G. Wei, N.P. Stern. *Dept. of Physics and Astronomy, and Applied Physics Program, Northwestern University, USA.*
10:42-11:00	**Break**	**Break**

	(Room A) STM Manipulation *Session Chair:* ***J.R. Guest*** *(CNM-ANL)*	**(Room B) Piezoelectric and New Instrumentations** *Session Chair:* ***S. Darling*** *(CNM-ANL)*
11:00-11:18	Dangling bond dimer on Ge(001):H surface: prototypical system for atomic and molecular switching. S. Godlewski, **M. Kolmer**, H. Kawai, R. Zuzak, B. Such, J. Lis, M. Saeys, P. de Mendoza, A. M. Echavarren, C. Joachim, M. Szymonski. *Dept of Physics of Nanostructures and Nanotechnology, Jagiellonian University, Krakow, Poland, IMRE and Dept. of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, CEMES-CNRS,Toulouse, France, and Institute of Chemical Research of Catalonia, Tarragona, Spain*.	(**Invited**) Charge gradient microscopy: high-speed visualization of polarization charges using a nanoscale probe. **S. Hong**, S. Tong, W.I. Park, Y. Hiranaga, Y. Cho, A. Roelofs. *Materials Science Division and [b]Nanoscience and Technology Division, Argonne National Laboratory, USA, and Research Institute of Electrical Communication, Tohoku University, Japan.*
11:18-11:36	Lateral motion of CO on Ag(110) surface via vibrational excitation by tunneling electron. **J. Oh**, H. Lim, J. Jung, Y. Kim. *Surface and Interface Science Laboratory, RIKEN, Japan, and IBS Center for Multidimensional Carbon Materials, UNIST, Ulsan.*	Invited talk continued.
11:36-11:54	Incorporation of metal-organic molecules into artificial nano-cavities in metal surfaces by STM manipulations. **A.DiLullo**, Y. Li, B. Fisher, S.-W. Hla *Argonne National Laboratory, and Ohio Univ., USA.*	Enhancement of local piezoresponse in polymer ferroelectrics via nanoscale control of microstructure. **Y.-Y. Choi**, P. Sharma, C. Phatak, **D. J. Gosztola,** Y. Liu, J. Lee, J. Li, A. Gruverman, S. Ducharme, S. Hong. *Materials Science Division, and Center for Nanoscale Materials Argonne National Laboratory, Dept. of Physics and Astronomy, Univ. of Nebraska, USA, Faculty of Materials, Optoelectronics and Physics, Xiangtan University, P. R. China, Dept. of Mechanical Engineering, University of Washington,USA.*
11:54-12:12	Lateral switching of a CO by vibrational excitation. H. J. Yang, M. Kawai, **Y. Kim** *RIKEN, and the University of Tokyo, Japan.*	Introducing nano-FTIR – infrared imaging and spectroscopy at 10nm spatial resolution. **T.Gokus**, F. Huth, M. Diem, S. Schiefer, A.J.Huber. *Neaspec GmbH, Germany.*
12:12-14:30	**Lunch Break**	**Lunch Break**

	(Room A) Nanomagnetism *Session Chair:* ***T. Jung*** *(PSI, Switzerland)*	**(Room B) Nano-optics** *Session Chair:* ***R. Winarski*** *(ANL)*
14:30-14:48	(**Invited**) Scanning tunneling microscopy of iron on manganese nitride and on gallium nitride surfaces. A.-O. Mandru, W. Lin, **A.R. Smith**, H.A.H. Al-Brithen, J.G. Sanchez, N. Takeuchi. *Nanoscale & Quantum Phenomena Institute, Dept. of Physics & Astronomy, Ohio Univ., USA, Benemèrita Universidad Autònoma de Puebla, Inst. de Física "Ing Luis Rivera Terrazas", and, Centro de Nanociencias y Nanotecnologia, Universidad Nacional Autònoma de Mèxico, Mèxico*	(**Invited**) Probing ultrafast spin dynamics by optical pump-probe STM. **H. Shigekawa** *Faculty of Pure and Applied Science, University of Tsukuba, Japan.*
14:48-15:06	Invited talk continued.	Invited talk continued.
15:06-15:24	Tuning magnetic anisotropy and Kondo screening in a Hund's impurity by controlled hydrogenation. A. A. Khajetoorians, **M. Steinbrecher**, M. Valentyuk, T. Schlenk, A. Lichtenstein, T. O. Wehling, J. Wiebe, R. Wiesendanger. *Inst. of Applied Physics, Hamburg University, and Inst. of Theoretical Physics, Hamburg University, Germany.*	Optical processes in isolated phthalocyanines probed by scanning tunneling luminescence spectroscopy. **H. Imada**, M. Imai[1], T. K. Shimizu, M. Kawai, Y. Kim.*Surface and Interface Science Laboratory, RIKEN, Dept. of Advanced Materials Science, The University of Tokyo, and National Institute for Materials Science, Tsukuba, Japan.*
15:24-15:42	Reversible control of single molecule Kondo interactions. **Y. Li**, A. DiLullo, B. Fisher, S.W. Hla. *Argonne National Laboratory, and Ohio University, USA.*	Cathodoluminescence of plasmonic crystals and cavities. **N. Yamamoto**, H. Saito. *Tokyo Institute of Technology, Tokyo, and JST-CREST, Saitama, Japan.*

Conference Dinner

Time and Location TBA.

Thursday (31 July 2014)

8:30-9:15 **Plenary**	*Session Chair:* ***S.W. Hla*** *(ANL/Ohio Univ.)* **P. Littlewood** (*Argonne National Laboratory, USA).*
9:15-9:30	**Break**
	(Room A) Nanoscale Superconductivity *Session Chair:* ***S.W. Hla*** *(ANL/Ohio Univ.)*
9:30-10:06	(**Invited**) Scanning tunneling spectroscopy of single crystal superconductors and molecular adsorbates. **K. J. Franke** *Fachbereich Physik, Freie Universität Berlin, Germany.*
10:06-10:24	Real-space observations of superconducting proximity effect by scanning tunneling microscopy and spectroscopy. **H. Kim**, S.-Z. Lin, M.J. Graf, T. Kato, Y. Hasegawa. *Inst. for Solid State Physics, University of Tokyo, Japan, and Theoretical Division, Los Alamos National Laboratory, USA.*
10:24-10:42	A superconducting raft in the Fermi sea. **K. Z. Latt**, S. Khan, H. Chang, A. Hassanien, S.-W. Hla. *Nanoscale and Quantum Phenomena Institute, Physics & Astronomy Dept., Ohio Univ., USA, National Institute of Chemistry, Ljubljana, Slovenia, Center for Nanoscale Materials, Argonne National Laboratory, USA.*
10:42-11:00	**Break**

	(Room A) 2-D Nanostructures *Session Chair:* ***N. Guisinger*** *(ANL)*
11:00-11:36	Prospects for hydrogen storage in graphene. **S. Heun**. *NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Pisa, Italy.*
11:36-11:54	First principles analysis of defect-mediated Li adsorption on graphene. **H. Yildirim**, Z. Zhao, A. Kinaci, M.K.Y. Chan, J.P. Greeley. *Purdue University, School of Chemical Engineering Dept., and Center for Nanoscale Materials, Argonne National Laboratory, USA.*
11:54-12:12	Molecular sensing at graphene grain boundaries. **P. Yasaei**, B. Kumar, A. Baskin, N. Repnin, P. Král, A. Salehi-Khojin. *Dept. of Mechanical and Industrial Engineering, and Dept. of Chemistry, University of Illinois at Chicago,USA.*

12:12-12:30	**Introduction to NSS-9**
	Closing Remarks

28 July 2014 Monday (Morning Sessions)

[Plenary] Complex Spin States Revealed and Locally Manipulated by 3D-Vector Resolved Spin-Polarized Tunneling Techniques

Roland Wiesendanger*

Institute of Applied Physics and Interdisciplinary Nanoscience Center Hamburg
University of Hamburg, D-20355 Hamburg, Germany

Magnetism in ultrathin films can significantly deviate from commonly known bulk magnetism due to low dimensionality, hybridization effects, changes of the lattice constant, stacking dependencies, and broken inversion symmetry at interfaces. This can lead to complex non-collinear spin states such as spin spirals or skyrmions. Especially magnetic skyrmions with their non-trivial topology are interesting objects for both fundamental as well as application-oriented research due to their possible utilization in future magnetic data storage.

Based on the development of atomic-resolution spin-polarized scanning tunneling microscopy (SP-STM) and spectroscopy [1], operated within 3D superconducting magnet systems, we have discovered nanoskyrmion lattices in single atomic layers of transition metals on particular substrates exhibiting a large spin-orbit coupling, such as monolayer (ML) Fe films on Ir(111) [2]. In this case, skyrmionic lattices with a periodicity of only one nanometer can be stabilized even in zero external field by the Dzyaloshinskii-Moriya interaction combined with the breaking of inversion symmetry at surfaces and interfaces. Temperature-dependent SP-STM studies have shown that the skyrmion lattice of 1 ML Fe/Ir(111) is stable against thermal agitation up to T = 27.7 K. Further elevating T to 28.0 K results in a fading of the magnetic SP-STM contrast, indicating a phase transition into the paramagnetic state.

More recently, we have made use of multiple interface engineering in bilayer and multilayer systems in order to demonstrate the direct observation and manipulation of individual skyrmions of single-digit nanometer-scale size [3]. By locally injecting spin-polarized electrons from an atomically sharp SP-STM tip, we were able to write and delete individual skyrmions one-by-one, making use of spin-transfer torque exerted by the injected high-energy spin-polarized electrons [4]. An external magnetic field was used to tune the energy landscape, and the temperature was adjusted to prevent thermally activated switching between topologically distinct states. Switching rate and direction can then be controlled by the parameters used for current injection. The creation and annihilation of individual magnetic skyrmions demonstrates their great potential for future nanospintronic devices making use of individual topological charges as information carriers [5].

References

[1] R. Wiesendanger, Rev. Mod. Phys. **81**, 1495 (2009).
[2] S. Heinze et al., Nature Physics **7**, 713 (2011).
[3] N. Romming et al., Science **341**, 6146 (2013).
[4] S. Krause et al., Science **317**, 1537 (2007).
[5] A. Fert et al., Nature Nanotechnology **8**, 152 (2013).

*Corresponding author: wiesendanger@physnet.uni-hamburg.de

Work in collaboration with: K. von Bergmann, S. Blügel, J. Hagemeister, Ch. Hanneken, S. Heinze, J. Hermenau, S. Krause, A. Kubetzka, M. Menzel, N. Romming, A. Sonntag, and E. Vedmedenko.

[Invited] Nanowires as a generic technology for science and applications

L. Samuelson[1,2]

[1]Lund University, Solid State Physics & Nanometer Structure Consortium, Lund, Sweden
[2]QuNano AB, Glo AB & Sol Voltaics AB, Ideon Science Park, Lund, Sweden

Very often, progress in science and technology comes as consequences of new achievements in materials science and technology. I will here describe one such technology step related to the realization of guided self-assembly for the growth of semiconductor nanowires [1-3]. Beside the obvious importance this has had for materials science, this has also enabled progress in many other areas of science and technology, such as in low-dimensional physics, in life-science, in nanoelectronics as well as in energy and optoelectronics applications [4-8]. I will in this talk review the development of the field of semiconductor nanowires and indicate the opportunities it offers for future applications especially related to energy and optoelectronic applications.

References

[1]. B.J. Ohlsson et al., “Size-, shape-, and position-controlled GaAs nano-whiskers”, Appl. Phys. Lett. **79**, 3335 (2001)
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[Invited] Electronic structure and exciton formation at ZnO interfaces

Martin Wolf

Department of Physical Chemistry, Fritz-Haber-Institute, Berlin, Germany

The combination of inorganic semiconductors with organic molecules to hybrid systems promises superior functionality of the interface compared to optoelectronic properties of the single materials. We have investigated the electron dynamics of the ZnO(10-10) surface and the influence of hydrogen and several organic molecules on the electronic structure using time-resolved two-photon-photoemission (2PPE) spectroscopy. Hydrogen termination leads to the formation a metallic ZnO surface, whereas e.g. by pyridine adsorption a substantial work function reduction up to 2.9 eV is achieved, which can be useful controlling the energy level alignment at inorganic/organic interfaces. By exploiting femtosecond time resolution in 2PPE spectroscopy we directly monitor the hot electron relaxation in the ZnO conduction band and the formation of an excitonic state at the ZnO surface within a few ps (see Fig. 1), which decays via a thermal activated process on a 100 ps timescale.

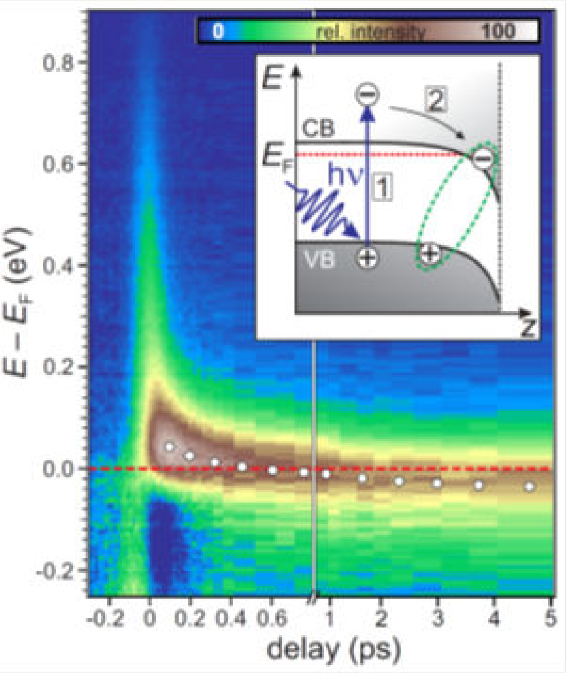

Fig. 1 *Relaxation of photoexcited electrons and dynamics of exciton formation at the hydrogen terminated ZnO(10-10) surface*

Furthermore, we report first results of tip-enhanced Raman spectroscopy (TERS) under ultra-high vacuum conditions for graphene nanoribbons (GNRs) fabricated on Au(111) by an on-surface polymerization technique. The 0.74 nm wide armchair GNRs are directly observed by scanning tunneling microscopy at room temperature and the characteristic vibrational modes of GNRs appear in both, the far-field and the tip-enhanced near-field Raman spectra. In the near-field Raman scattering is enhanced by up to 4×10^5, while strong intensity fluctuations (blinking) frequently emerge in the time series of the tip-enhanced Raman spectra. This blinking is attributed to originate predominantly from thermal fluctuations of the effective radius of the Au tip apex that induces the localized plasmonic field.

Acknowledgements: This work was performed in collaboration with J.-Ch. Deinert, D. Wegkamp, M. Meyer, C. Richter, J. Stähler, T. Kumagai (Fritz Haber Institute, Berlin) and A. Shiotari (Kyoto Univ., Japan)

[Invited] Functional Nanomaterial Heterostructures

M. C. Hersam[1]

[1]*Materials Science and Engineering Dept., Northwestern University, Evanston, IL 60208 USA*

Improvements in nanomaterial monodispersity have yielded corresponding enhancements in the performance of electronic, optoelectronic, sensing, and energy technologies [1,2]. However, in all of these cases, 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 [3]. Similarly, nanostructured organic assemblies [4] and atomic oxygen functionalization [5] allow one-dimensional [6] and zero-dimensional [7] oxide nanostructures, respectively, to be templated in a manner that maintains the superlative properties of the underlying graphene. In another example, 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 10^6 while concurrently achieving mobilities of ~150 $cm^2/V\text{-}s$ [8]. By utilizing unconventional gate electrode materials (e.g., Ni), the threshold voltage of semiconducting CNT TFTs can be further tuned, thus enabling the realization of CNT CMOS logic gates with sub-nanowatt static power dissipation and full rail-to-rail voltage swing [9]. Finally, p-type semiconducting CNT thin films are integrated with n-type single-layer MoS_2 to form p-n heterojunction diodes [10]. 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 nanomaterial-based electronic and optoelectronic applications can be substantially enhanced and diversified into new areas through precise integration into heterostructure devices.

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Three Dimensional Graphene-Gold Nanoparticles Hybrid Structure for Surface Enhanced Raman Spectroscopy

Juyoung Leem[1], Michael Cai Wang[1], and SungWoo Nam[1]

[1]*Department of Mechanical Science and Engineering,*
University of Illinois at Urbana-Champaign, Urbana, IL 60801, USA

Graphene is a two dimensional (2D) sp^2 bonded carbon crystal with delocalized π electrons contributing to surface enhanced Raman scattering (SERS) in a way of chemical mechanism (CM) [1]. Furthermore, orders-of-magnitude stronger Raman enhancement has been achieved by a hybrid structure of gold nanoparticles (Au NPs) decorated with a flat graphene layer [2] due to electromagnetic (EM) field enhancement of Au NPs. To further improve SERS of graphene-Au hybrid structures by introducing three-dimensionality, we propose a three-dimensional (3D) SERS platform based on crumpled graphene structure decorated with Au NPs. First, we demonstrate controlling of the decoration of Au NPs on graphene surfaces with tunable NP sizes and thus plasmonic resonance wavelengths. Second, we induce controlled crumpling of graphene-Au NPs hybrid structures to generate 3D textured surfaces with enhanced CM and EM field enhancement. We finally investigate SERS enhancement effects of our 3D graphene-Au NPs hybrid structures by using several key Raman active molecules. We believe our new 3D graphene-Au NP hybrid platform will provide new and enhanced SERS detection capabilities of small molecules for advanced biomedical diagnostics in the future.

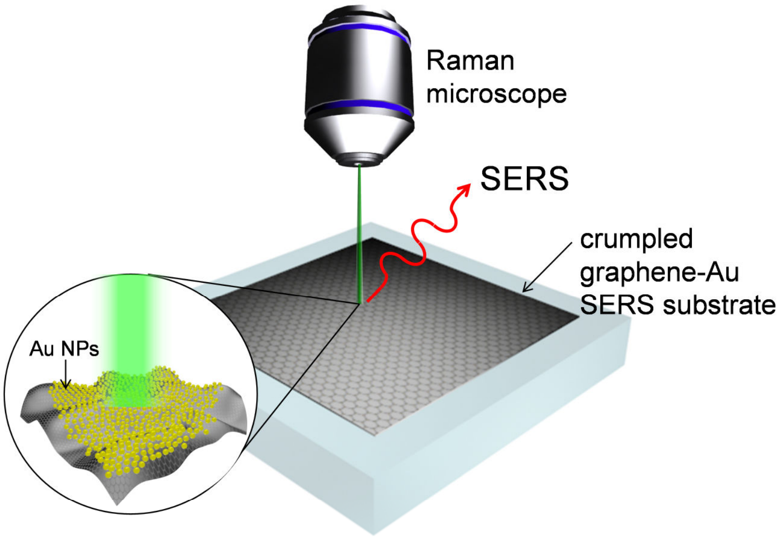

Fig. 1: *A schematic drawing of 3D graphene-Au NPs structure for SERS applications.*

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Three-dimensional Textured Graphene Bioelectronics

Michael Cai Wang[1], SungGyu Chun[1] and SungWoo Nam[1,2]

[1]Mechanical Science and Engineering, [2]Materials Science and Engineering,
University of Illinois, Urbana-Champaign, Urbana, IL 61801, USA

Superb electromechanical properties of graphene, where large elastic deformation is achievable without significant perturbation of electrical properties, provide a substantial promise for flexible electronics, advanced nanoelectromechanical and bioelectronic devices. We report three-dimensional (3D) field-effect transistor biosensors built from the monolithic integration of crumpled graphene and graphite. First, we present monolithic synthesis of graphene-graphite for all-carbon bioelectronic transistor arrays [1, 2]. Second, we develop a rapid and scalable method of texturing 2-dimensional (2D) graphene by using soft-matter transformation of shape-memory polymers into 3D bioelectronic sensors. We demonstrate that the thermally-induced transformation of graphene on a polymeric substrate creates 3D textured graphene. Quantitative analysis shows that both the wavelength and height of textured graphene are a few micrometers at an applied strain of 300% and that the 3-dimensionality of graphene (i.e., wavelength and height of texturing) can be controlled by the processing parameters. We further characterize the electrical and mechanical properties of 3D graphene, and demonstrate the robust electromechanical properties of 3D textured graphene. Finally, we explore biosensor device applications by constructing an array of field-effect biosensors. We believe our approach to forming textured graphene by soft-matter transformation offers a unique avenue for creating advanced and 3D bioelectronic devices, and furthermore, these unique capabilities could be exploited in chemical and biological detection and conformal interface with biological systems in the future.

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[Invited] Pico-imaging by X-ray-Induced Effects using SR-based STM

Akira Saito[1,2], Y.Furudate[1,2], Y.Kusui[1,2], T.Saito[1,2], M.Akai-Kasaya[1], Y.Tanaka[2], K.Tamasaku[2], Y.Kohmura[2], T.Ishikawa[2], Y.Kuwahara[1,2] and M.Aono[3]

[1] *Dept. Precision Sci.& Technol.,Graduate School of Engineering, Osaka Univ.,Osaka, Japan*
[2] *RIKEN SPring-8 Center, Sayo-cho, Hyogo, Japan*
[3] *National Inst. for Materials Science, Tsukuba, Ibaraki, Japan*

Scanning tunneling microscopy (STM) combined with brilliant X-rays from synchrotron radiation (SR) enabled the elemental analysis on solid surfaces at an atomic scale. The principle of the analysis is based on the inner-shell excitation of an element-specific energy level “under STM observation”. A key to obtain an atomic locality is to extract the element- specific modulation of the local tunneling current (not emission that can damage the spatial resolution), which is derived from the inner-shell excitation [1].

After successes in the elemental analyses by SR-STM [1,2] on a semiconductor hetero-interface (Ge on Si) and metal-semiconductor interface (Cu on Ge), we attempted new sample with a metallic substrate (Co on Au) to evaluate the principle and generality of the elemental contrast by this method.

We have succeeded in obtaining the elemental contrast between Co and Au (Fig.1), where several specific features were found in the elemental contrast image. The results on the metallic substrate suggest the generality of the method and give some important implications on the principle of contrast. For all cases of three samples, the spatial resolution of the analysis was estimated to be ~1 nm or less, and it is worth noting that the measured surface domains had a deposition thickness of less than one atomic layer (Fig.1).

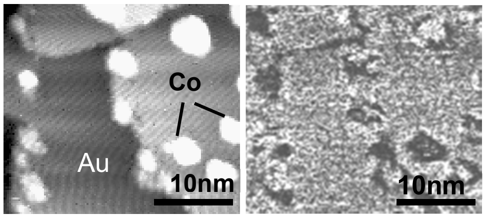
(a) Topographic **(b)** Element contrast

Fig.1 *(a)Topographic image, (b) beam-induced tip current image of Au(111)-Co (1.5V, 0.2 nA). X-ray energy= 7.740 keV (> Co K-edge)*

On the other hand, we found that the “X-ray induced atomic motion” can be observed directly with atomic scale using the SR-STM system effectively under the incident photon density of ~2 x10^{15} photon/sec/mm^2 [3]. SR-STM visualized successfully the track of the atomic motion (Fig.2), which enabled the further analysis on the mechanism of the atomic motion. It is worth comparing our results with past conventional thermal STM observations on the same surface [4], where the atomic motion was found to occur in the 2-dimensional domain. However, our results show the atomic track having a local chain distribution [3].

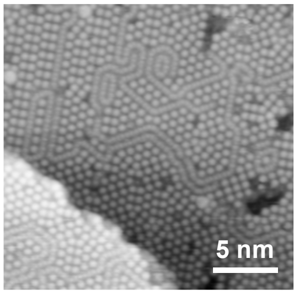

Fig.2 *X-ray-induced atomic motion tracks on Ge(111) that were newly imaged by the SR-STM system.*

The above mentioned results will allow us to investigate the chemical analysis and control of the local reaction with the spatial resolution of STM, giving hope of wide applications.

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Low Temperature Synchrotron X-ray Scanning Tunneling Microscopy (LT-SXSTM)

N. Shirato[1], H. Kersell[2], C. Preissner[1], S.-W. Hla[2,3], and V. Rose[1,3]

[1]X-ray Science Division, Argonne National Laboratory, Argonne IL 60439
[2]Department of Physics and Astronomy, Ohio University, Athens, OH 45701
[3]Center for Nanoscale Materials, Argonne National Laboratory, Argonne IL 60439

Low temperature scanning tunneling microscopy (LT-STM) combined with synchrotron based X-rays provides a new tool to capture chemical interactions and magnetic spin states on surfaces at high spatial resolution. The technique will drastically increase the spatial resolution, and it measures chemical and magnetic information along with surface topography. Here, we will present the current status of the ongoing development of a LT-SXSTM. Compared to our previous generation microscopes [1], the new system features, i.e. 4 degrees of freedom stages for the sample and tip alignment with respect to the X-ray beam, in-house developed LabVIEW and MATLAB based data acquisition and analysis software, 6-axis active vibration isolation system and low temperature capability down to 4 Kelvin using a liquid Helium flow cryostat.

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Synchrotron X-ray Scanning Tunneling Microscopy (SXSTM) at the Advanced Photon Source

M. Cummings[1], N. Shirato[1], B. Stripe[1], C. Preissner[1], D. Rosenmann[2], S.-W. Hla[2], V. Rose[1,2]

[1] *Advanced Photon Source*
[2] *Center for Nanoscale Materials*

The synchrotron x-ray scanning tunneling microscope (SXSTM) is a new in-situ, high-resolution microscope technique, being developed at the Advanced Photon Source. The microscope images nano-scale materials at the surface with chemical, electronic, and magnetic contrast, taking full advantage of the chemical, electronic and magnetic sensitivities that synchrotron radiation offers, and combines these radiological sensitivities with the sub-nanometer spatial resolution that scanning tunneling microscopes attain [1].

Successful nanometer-scale, elemental contrast has been demonstrated with SXSTM instrumentation. The elemental sensitivity, demonstrated by this technique, was accomplished by placing a chopper system upstream of the SXSTM instrument. The chopper system modulates the incoming monochromatic beam of radiation, on and off, at a frequency of 3 kHz. By inserting an electronic lock-in amplifier and a topographic low-pass filter downstream, a modulated current signal, generated at the tip of the scanning tunneling microscope, can be de-convoluted into its component parts: (i) the chemical signal and (ii) the topographic signal. These latest developments in the SXSTM instrumentation will prove powerful in surface characterization and will enhance our understanding of nano-scale physical phenomena at the surface.

This work was funded by the Office of Science Early Career Research Program through the Division of Scientific User Facilities, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant SC70705. Work at the Advanced Photon Source, the Center for Nanoscale Materials, and the Electron Microscopy Center was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

[1] http://www.aps.anl.gov/Xray_Science_Division/Sxspm/
[2] U.S. Patent Application 13/791,157

28 July 2014 Monday (Afternoon Sessions)

[Invited] TiO$_2$ Biocomposites within Cell Machinery

Tamara Koritarov,* Vani Konda,[#] Riba Mustafi,[#] Marc Bissonnett,e[#] Tijana Rajh*
**Center for Nanoscale Materials, Argonne National Laboratory, 9700 S Cass Ave, Argonne IL 60540;*
[#]Department of Medicine, The University of Chicago Medicine, 5841 S. Maryland Avenue, MC 4076, Chicago, IL 60637

Semiconductor photocatalysis using nanoparticlate TiO$_2$ has proven to be a promising technology for use in photocatalytic reactions, in nanocrystalline solar cells, and is of considerable interest for biomedical applications because of its potocatalytic efficiency and inherent stability. Herein we investigate the use of TiO$_2$ nanoparticles to manipulate the living cells. Reconstructed surfaces of metal oxide nanoparticles differ from the bulk by the presence of highly reactive under-coordinated surface. This can be used for their conjugation to biomolecules, as surface metal atoms exhibits high affinity for oxygen-containing ligands such as dopamine derivatives were employed as "leads" that bridge electronic properties of TiO$_2$ to electroactive biomolecules such as peptides or proteins, and to improve their optical properties in the visible region (TiDoL).[1] We have utilized monoclonal anti-EGFR antibodies (C225) for targeting of the TiO$_2$ and TiDoL nanoparticles to the specific cells such as epithelial colon cancer cells (HCT116). Photoinduced charge separation was than employed to create reactive oxygen species (ROS) and induce apoptosis in the tumor cells. Nanoconjugate synthesis protocols were optimized for *in vitro* and *in vivo* tumor treatment. C225 antibodies were utilized to recognize EGFR expressed at the surface of the colorectal cancer cells and increase retention of nanocomposites at disease-associated epitopes. On the other hand, photocatalytic properties of nanoparticles were used to induce apoptosis of cells affected by the disease upon illumination while leaving healthy cells intact. Following the light exposure the cells started showing typical morphological changes associated with apoptosis such as the formation of membrane-enclosed apoptotic bodies caused by budding of the cell membrane that contain the cytosol and well-preserved organelles (Fig. 1). This is important as apoptotic cells can be phagocytosed by macrophages and their fragments are rapidly cleared before cellular contents have enter the extracellular fluid, not eliciting an inflammatory response in the host.

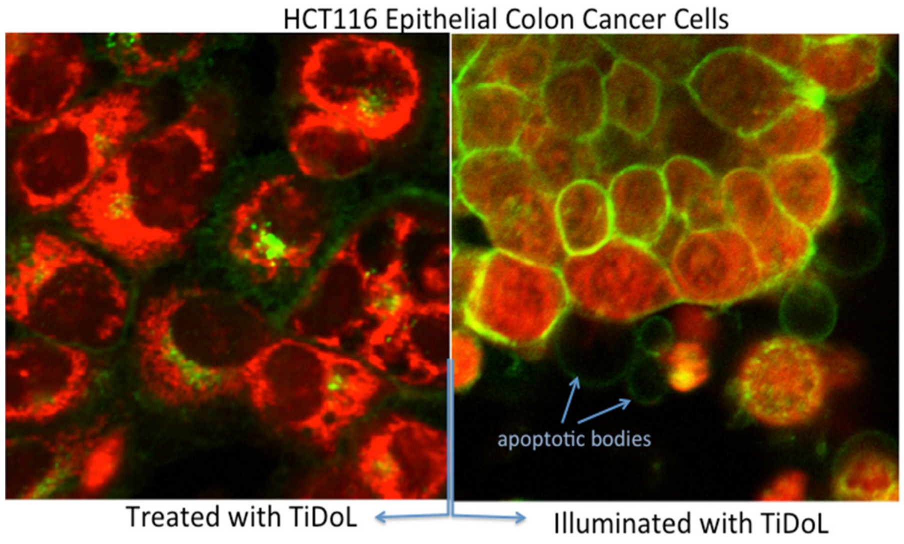

Fig.1. Fluorescence images of a HCT116 cells treated with TiDoL (TiO2-DOPAC-peptide) (left) and after illumination with 480 nm laser for 15 min.

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The Correlation between Cytoskeletal Structure and Cell Mechanics in Human Pulmonary Artery Endothelial Cells

Xin Wang[1], Mary E. Brown[2], Reiner Bleher[1], Steven Dudek[2], Gajendra S. Shekhawat[1], Vinayak P. Dravid[1]

[1]*Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA. 60208*
[2]*Department of Medicine, University of Illinois, Chicago, IL, USA. 60612*

Understanding cell mechanics is becoming increasingly important for disease diagnostics and therapeutic development. Acute lung injury (ALI) syndromes have high mortality rates in patients and are marked by disruption of the endothelial barrier in pulmonary blood vessels leading to edema and respiratory failure. In this study mechanical properties changing measured using AFM (atomic force microscopy) is correlated to cytoskeletal rearrangements within single cells directly observed using STEM (scanning transmission electron microscopy) in different physiological conditions. Thrombin increases cytoplasmic stress fiber formation, decreases the elastic modulus of the cell periphery, and opens intercellular gaps. In contrast, S1P (sphingosine 1-phosphate) induces formation of an actin cytoskeleton ring, significantly increases the elastic modulus of the cell periphery, and closes intercellular gaps. These observations provide biomechanics insights into how endothelial barrier function is modulated.

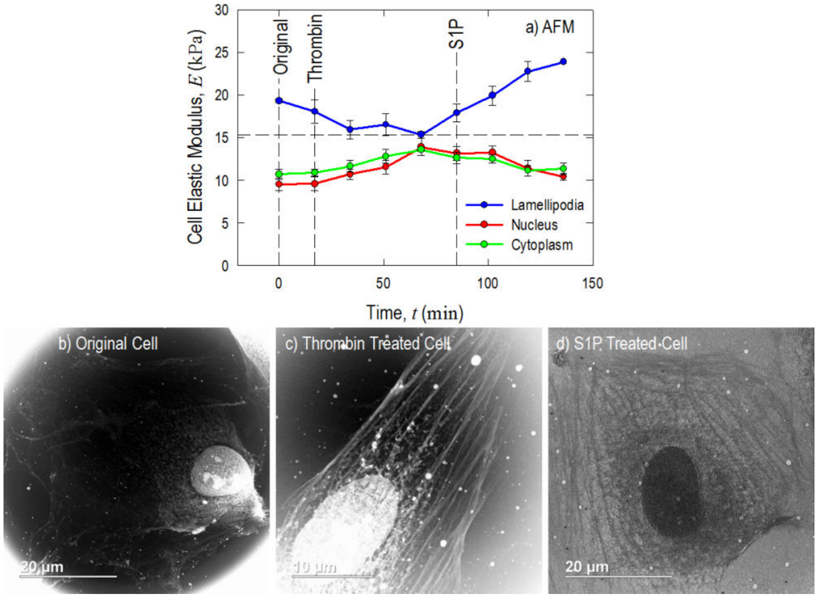

Fig. 1: *The correlation between mechanical properties of single cell with cytoskeletal structure re-arrangement within cell. (a) Mechanical properties of different parts of a single cell using AFM. (b) - (d) cytoskeletal structure of original cell, thrombin treated cell, and S1P treated cell using STEM.*

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Bacteria at the Nanoscale – Bacterial Stress Response Investigated by X-Ray Fluorescence and X-Ray Microscopy

R. Heine[1], Y. Yang[1], S. Kirchen[2], R. Debastiani[1], T. Gorniak[2,3], T. Senkbeil[2,3],
A. Rosenhahn[3], F. Xu[1], H. Suhonen[4], L. Helfen[4], C. Bartels[5], I. Wacker[5], Y.F. Song[6],
C.C. Wang[6], B. Stripe[7], V. Rose[7], M. Grunze[8], T. Schwartz[2], T. Baumbach[1].

[1]ANKA/IPS, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
[2]IFG, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
[3]Analytical Chemistry - Biointerfaces, Ruhr-University Bochum, 44780 Bochum, Germany
[4]ESRF – The European Synchrotron, 38043 Grenoble, France
[5]CryoEM, Center for Advanced Materials (CAM), 69120 Heidelberg, Germany
[6]NSRRC – Hsinchu 30076, Taiwan
[7]Argonne National Laboratory, Argonne, IL 60439, USA
[8]APC, University of Heidelberg, 69120 Heidelberg, Germany

Bacteria and bacterial biofilms might develop an increased robustness against antimicrobial agents and thus are of major concern in medicine and in many commercial enterprises. Especially the so-called VBNC (viable but nonculturable) state [1] is most dangerous, since in this condition the bacteria are not detectable with conventional microbiological cultivation methods but can resuscitate and cause new infections [2,3]. The VBNC state is a survival strategy of bacteria under toxic and stress conditions (adverse conditions of temperature, nutrient, or light) [4]; however, the biochemical mechanisms which lead to the high resistance and enable the bacteria to regrow even after extended periods of hibernation are still unknown.

We investigated the morphology and elemental composition of bacterial aggregates on interfaces by synchrotron radiation-based hard X-ray microscopy techniques. Microtomography experiments using full-field transmission X-ray microscopy (TXM) [5] with Zernike phase contrast were performed on different biofilm-habitat interfaces to explore the three-dimensional organization of the biofilm. Stress response mechanisms including relevant trace elements and their spatial distribution within individual bacteria were studied by correlative imaging with hard X-ray phase contrast tomography (holotomography) [6] combined with hard X-ray fluorescence (XRF) microscopy [7] with tens of nanometers resolution and sub-ppm sensitivity, and we observed a variation of elemental distribution in different physiological stages. This complementary information may provide clues about the microbial metabolism under stress conditions and possible defense mechanisms of the cells.

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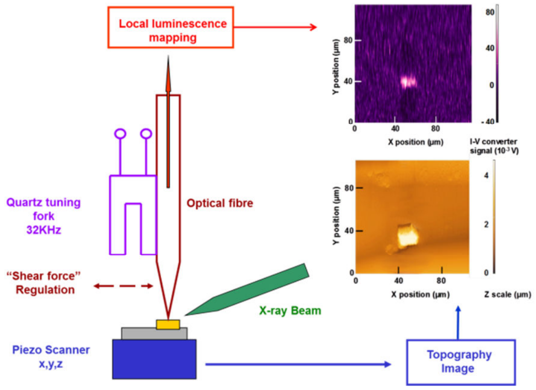
[Invited] Nanometer scale resolution topography combined to local photon spectroscopy

C. Fauquet[1], H. Maradj[1], M. Dehlinger[1], A. Erko[2], A. Bjeoumikhov[3], D. Tonneau[1]

[1]Aix-Marseille Univ., CINaM, 13288, Marseille, France
CNRS-UMR7325, 13288 Marseille, France
[2] Institute for Nanometre Optics and Technology, Helmholtz-Zentrum Berlin, Albert Einstein Straße, 15, 12489 Berlin, Germany
[3]IFG-GmbH, Rudower Chaussee 29/31, 12489 Berlin, Germany

Scanning Probe Microscopes are powerful tools to get surface topography at high lateral resolution. However these techniques cannot provide elemental chemical analysis. This represents a strong limitation for industrial applications. X-ray spectroscopies are very accurate techniques allowing to define the chemical composition and atomic structure of a sample. The lateral resolution of the techniques is limited by the primary X-ray beam size and can reach about 30 nm on advanced synchrotron beamlines. One major drawback of these techniques is that it is not possible to position the primary spot on a peculiar area on the sample, for example to spot and analyze a single nano-object.

We have designed and fabricated a Shear Force Microscope equipment (see figure) allowing to simultaneously obtain the sample topography and the local visible luminescence mapping [1] or the local XAS-XEOL [2] in ambient conditions. A sharp optical fibre is used as shear force probe for sample topography acquisition and for simultaneous collection of the visible luminescence under focused X-ray excitation (resolution 50 to 100 nm for both topography and chemical analysis). The equipment was fitted to a synchrotron beamline at ESRF as well as to low power micro X-ray source. Micro- and nano-particles were characterized with the equipment. Results will be presented.



Local sample X-ray Fluorescence collection allows to enlarge the variety of materials that could be characterized with the equipment. In this case, the sharp optical fibre is replaced by X-ray capillary optics. A test-bed was developed to show the concept feasibility. Simulations were performed to define the ultimate lateral resolution that can be achieved with such apparatus.

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Fabrication and Characterization of Smart CNT-based Tips for Synchrotron Assisted STM

Hui Yan[1], Marvin Cummings[2], Fernando Camilo[3], Daniel Rosenmann[2], Ming Lu[3], Xiao Tong[3], Weihe Xu[1], Volker Rose[2], Evgeny Nazareski[1]

[1]Brookhaven National Laboratory, 2 Center Street, Upton, NY, USA
[2]Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL, USA
[3]CFN, Brookhaven National Laboratory, 2 Center Street, Upton, NY, USA

Fundamental understanding of materials is a key to design, manipulate, and control their ultimate functionalities. Determination of atomic level chemical composition and atomic scale imaging become critical in order to develop materials by design. Synchrotron assisted STM (SXSTM) is a promising new technique to achieve real space chemically specific atomic mapping. Chemical sensitivity of SXSTM relies on excitation of core electrons by incident X-rays when their energy is tuned to an absorption edge of a particular element. However, photoelectrons are also excited along with core-level electrons, they yield additional current and interfere with the tunneling current. Therefore, ‘smart STM tips’ have to be developed to reduce the background photoelectron current and improve ultimate resolution of SXSTM. We have developed a novel approach to fabrication of ‘smart tips’ based on carbon nanotubes (CNT). Our work is a joint research project between Argonne National Laboratory (ANL) and Brookhaven National Laboratory (BNL). CNTs are chemically inert to oxygen and water and consequently possess superior physical properties (stiff, better elastic properties, high aspect ratio), which makes them ideal candidates for fabrication of ‘smart tips’ and STM imaging. In our work, we present an entire nanofabrication process of CNT-based smart tips using PECVD and FIB-SEM. We also present characterization and performance evaluation of developed smart tips using SEM and STM techniques.

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Smart MIM Tips for Next-Generation X-ray Scanning Tunneling Microscopes

D. Rosenmann[1], M. Cummings[2], N. Shirato[2], D. Miller[1,3], R. Winarski[1], S-W. Hla[1,4], V. Rose[1,2],

[1]*Center for Nanoscale Materials, Argonne National Laboratory. Argonne, IL 60439, USA*
[2]*Advanced Photon Source, Argonne National Laboratory. Argonne, IL 60439, USA*
[3]*Electron Microscopy Center, Argonne National Laboratory. Argonne, IL 60439, USA*
[4]*Ohio University. Physics and Astronomy Department, Athens, Ohio 45701, USA*

Sharp probes are the cornerstone for high spatial resolution in scanning tunneling microscopy (STM). However, in light-assisted STM additional properties of the tips have to be considered.
In Synchrotron x-ray scanning tunneling microscopy (SX-STM), absorption of photons by the sample can excite electrons to unoccupied states close to the Fermi level. [1] The conducting tip, tunneling over the sample surface, can locally measure these excited electrons. However, in addition, due to the large surface area illuminated, a large number of photoelectrons would also be detected at the sidewall of a normal tip, drastically limiting the achievable spatial resolution. In order to overcome this limitation we have developed a new kind of sharp metal-insulator-metal (MIM) probes that are coated with coaxial insulating and metallic films and serve as nanoscale detectors. [2]
We will be discussing the development of specialized multilayer-coated tips with minimized conducting apex. These "smart tips" serve as nanoscale detectors and constitute an important achievement for the development of next-generation x-ray and other light-assisted microscopes.

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Fig. 1: *This insulator-coated "smart tip" confines the signal detection to a tiny region of a sample. The nanofabricated tips have been developed to improve the sensitivity of the SX-STM technique.*

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[Invited] SiC nanowires: a cytocompatible tool for nanomedicine

Giancarlo Salviati

IMEM-CNR, Parco Area delle Scienze 37/A, 43124 Parma, Italy

A new two-fold nanosystem exploiting the simultaneous action of oxidative stress generated by self lighted photodynamic therapy [1] and hyperthermia induced by radiofrequency magnetic fields [2], is presented and discussed in view of possible deep cancer treatments. The nanosystem is based on SiO_2/3C-SiC nanowires functionalized with tetraphenylporphyrins and superparamagnetic Fe_3O_4 nanoparticles [3]. Fe_3O_4 nanoparticles ($5<\phi<8$ nm) are prepared by thermal decomposition of iron acetylacetonate. The free hydroxy groups of the SiO_2 shell are properly functionalized and then Fe_3O_4 nanoparticles, after further stabilization (10-undecynoic acid), are grafted onto the nanowires by exploiting a click-chemistry reaction. The best superparamagnetic properties are found for 8 nm nanoparticles which present a saturation value of the magnetic moment per unit volume of 60 emu/gr. The specific power absorption (hyperthermia) of the same nanoparticles (f=250 KHz, H=0.016 T) is around 4.3 W/g, a value which allows the cell to achieve in 1100 sec a final T >43 °C. To verify the biocompatibility of the nanosystem, after optimizing the functional properties [4,5], in-vitro tests on lung and human breast adenocarcinoma cells and human skin derma fibroblasts are carried out. The influence of concentration (0-100 □g/ml) and time (up to 72 hrs) on cell proliferation and death is studied. It is found that SiO_2/SiC nanowires inhibit cell proliferation and induce necrosis only at concentrations >50-100 µg/ml. The Fe_3O_4 nanoparticles do not inhibit cell proliferation and do not induce death up to 100 μg/ml as well as oxidative stress up to 50 μg/ml. The self-lighted photodynamic effect is then tested on Lung adenocarcinoma cells after internalization of the complete nanosystem by an endocytosis process. After 72 hrs from irradiation in an X-Ray radiotherapic linear accelerator at 6 Gy, the death of the 75% of cancer cells is observed [6]. Finally the hyperthermic effect on the same cells after the complete system internalization is also observed.

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Visible luminescence of sulfur-doped micro-structured black silicon analyzed at the nanoscale

Filippo Fabbri[1,], Yu-Ting Lin[2], Matthew J. Smith[3], Eric Mazur[2,4], Silvija Gradecak[3] Giancarlo Salviati[1]
[1]*IMEM-CNR Institute, Parco Area delle Scienze 37/A, 43010, Parma, Italy*
[2] *School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.*
[3]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA*
[4] *Department of Physics HarvardUniversity, Cambridge, Massachusetts, USA.*

Silicon-based optoelectronic devices that operate at photon energies that are less than the silicon bandgap (1.1 eV) have been fabricated using femtosecond (fs) laser doping. This process drives concentrations of chalcogen atoms in silicon to levels several orders of magnitude beyond their equilibrium solubility limit and produces hyper-doped silicon that exhibits near-unity absorption in the infrared (IR) region, at wavelengths to which crystalline silicon is transparent. Such properties are not achievable through equilibrium doping techniques, and the ability to tune the band structure of silicon with fs-laser doping makes this process of great interest for IR-photodetectors and photovoltaics. Aside from the drastic change in the absorption properties, researchers also observed visible luminescence in silicon structured by femtosecond laser in air [1]. This broadband luminescence was attributed to the formation of SiOx and quantum confinement. To fully characterize and optimize the material in the pursuit of obtaining novel nanophotonics devices, we study the visible luminescence properties of sulfur-doped micro-structured black silicon by cathodoluminescence (CL) mapping and spectroscopy. We fabricate sulfur-hyperdoped micro-structured black silicon by irradiating a silicon (100) wafer with a train of Ti:Sapphire femtosecond laser pulses in an environment containing sulfur precursors (SF_6). Room-temperature SEM-CL spectroscopy reveals a broad emission, peaked at about 2.4 eV. This broad emission is composed of three main components: an emission at 2.7 eV related to silicon oxide oxygen deficiency center (SiODCII)[2], an emission at 2.4 eV attributed to the incorporation of sulfur in silicon oxide[3], and an emission at 1.9 eV related to the non-bridging oxygen hole center (NBOHC) [2]. This analysis reveals that the visible emission is related to an oxidation process occurred during the material processing. In addition CL panchromatic mapping studies reveal that the presence of microstructures (about the 4%) with an high emission yield. We have been able to study one of these microstructures in a transmission electron microscope (TEM) to evaluate the light emission properties at the nanoscale. A comparative study of TEM-CL (spectroscopy and panchromatic mapping) and energy disperse X-ray (spectroscopy and mapping) reveals the presence of SiOx pockets with a high light emission yield (Figure 1).

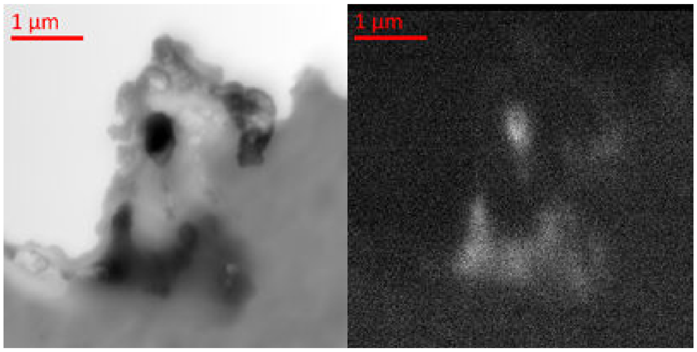

Fig. 1*(a) STEM Image of the micro-structured black silicon, (b) Panchromatic cathodoluminescence map., revealing high emission yield areas.*

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Electron Microscopy Evidences on Relevance of Microstructure - Property Correlations

Avanish Kumar Srivastava
National Physical Laboratory, Council of Scientific and Industrial Research
New Delhi 110 012. India
Email: aks@nplindia.org

The idea of present talk is to highlight the priority areas in synthesis, characterization and properties evaluation in the field of science and technology of nanostructured materials, as under investigation in the group. The research activity has been aimed for the development of newer materials and evaluation leading towards the optimization of process parameters for best possible applicability. In the present paper, few case studies on electron microscopic and spectroscopic studies of materials useful for energy, optical and sensing, have been presented and discussed. It has been established that nanostructuring of thermoelectric materials, important for energy, results in a clear enhancement in the figure-of-merit. It has been further demonstrated that the conducting grain boundaries due to inclusion of second phase particles in Mg_2Si/Pb system increase the ZT. There are significant differences in the properties of thermoelectric materials due to nanostructuring encompassing dense-grain boundaries, ultra-fine inclusions, lattice-scale modulations, etc., which in turn alter the performance of these fascinating class of materials for different energy applications. Another set of examples are taken up from the nanostructured ZnO, TiO_2, WO_3 and the allotropes of Carbon on novel routes of syntheses, microstructures, growth morphologies and related spectroscopic, optical and electrochemical performance. A few examples will be drawn from the magnetic materials dealing with difficulties and pursuance in the observations of magnetic micro- and nano- scaled features in addition to the conventional microstructures.

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[Invited] Exploring ZnO Nanostructures by Synchrotron-based Scanning X-ray and PhotoElectron Microscopes

M. K. Abyaneh[1], B. Bozzini[2], T. Araki[1], B. Kaulich[1]

[1]*Diamond Light Source Ltd., Harwell Science & Innovation Campus, Didcot, OX11 0DE, United Kingdom*

[2]*Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni s.n., 73100 Lecce, Italy*

Zinc Oxide (ZnO) based materials have found great attraction in the last few decades and are one of the most widely used functional inorganic oxides. ZnO, either in pure form or as a doped compound, is an appealing material for a wide range of applications, including supercapacitors, sensors, catalysis and optoelectronic applications. On the other hand, the complementary capabilities of synchrotron-based X-ray microscopes in terms of imaging, spectroscopy, spatial and time resolution and variable probing depths have opened unique opportunities to explore nano and micro-structure systems and provide chemical composition of these technologically relevant complex materials and correlate simulated systems to the actual operating conditions [1,2].

Novel approaches will be presented for synthesis of a) Prickly ZnO nanostructures [3] and b) ZnO Mn-Cu-doped hybrid materials [4] and their characterization using scanning photoelectron microscopy (SPEM) and scanning X-ray microscopy (SXM) techniques, respectively. Prickly nanostructures of ZnO have been obtained by the hydrothermal synthesis technique. Structures are analyzed using X-ray diffraction, electron microscopy as well as SPEM (ESCA-microscopy beamlines at Elettra, Italy). The analysis revealed that the prickly ZnO nanostructures are highly crystalline with hexagonal wurtzite phase and possess homogeneous compositional structures. These nanostructures exhibit intense near band-edge emission. Photoluminescence analysis showed that the structures also give defect-induced blue emission along with green emission.

The morphology, composition and chemical-state of pulse-plated Mn–Cu–ZnO, a prospective active material for supercapacitors, investigated using a combination of X-ray imaging with high lateral resolution X-ray fluorescence and X-ray absorption spectroscopies (at TwinMic, Elettra, Italy). The composition-morphology results are complemented by electrochemical measurements and numerical simulations. It has been found that pulse-plating allows the growth of Mn and Cu-doped ZnO with a self-organised and spatially consistent stable distribution of composition and chemical-state. Doping of ZnO layers is robust with respect to the local current density and electrodeposition leads spontaneously to the growth of hybrid composites, which are ideal supercapacitor electrodes that can be directly plated onto the current collectors.

Last part of the presentation will be dedicated to introduce the I08-SXM beamline at Diamond Light Source, UK, which is hosted a Scanning X-ray microscope with outstanding capabilities and features. I08-SXM is an instrument that covers a broad photon energy range (250 to 4200 eV) providing access to all major K- and L-absorption edges for SXM elemental and chemical analysis, with lateral resolutions down to ~20 nm depending on the imaging mode, combined with the high quality spectroscopic (NEXAFS) data for chemically-sensitive analysis, and X-ray fluorescence (XRF) mapping.

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[Invited] Nanotomographic Imaging Techniques at the Hard X-ray Nanoprobe

R. P. Winarski[1]

[1]Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL, 60439 USA

X-ray imaging techniques are being developed to visualize in-situ and in-operando behavior of materials. We have been developing new capabilities to allow us to capture changes in systems in real time using the brightness provided to us by the Hard X-ray Nanoprobe Beamline, with resolutions better than thirty nanometers [1,2]. We have developed techniques to image structural and elemental changes in a wide variety of materials, including battery electrodes, advanced cement composites, and electronic junctions [3-5]. In this presentation, I will be discussing how our techniques have been developed to explore dynamic behaviors in these systems, and in many cases see for the first time what is happening inside these materials while they are evolving.

The Hard X-ray Nanoprobe has the advantage of combining a variety of measurement techniques to understand the nature of a sample. The Hard X-ray Nanoprobe is a combination scanning probe and full-field imaging microscope that incorporates scanning fluorescence imaging, nanodiffraction, and transmission imaging with absorption and phase contrast. We now routinely use a combination of techniques to examine samples.

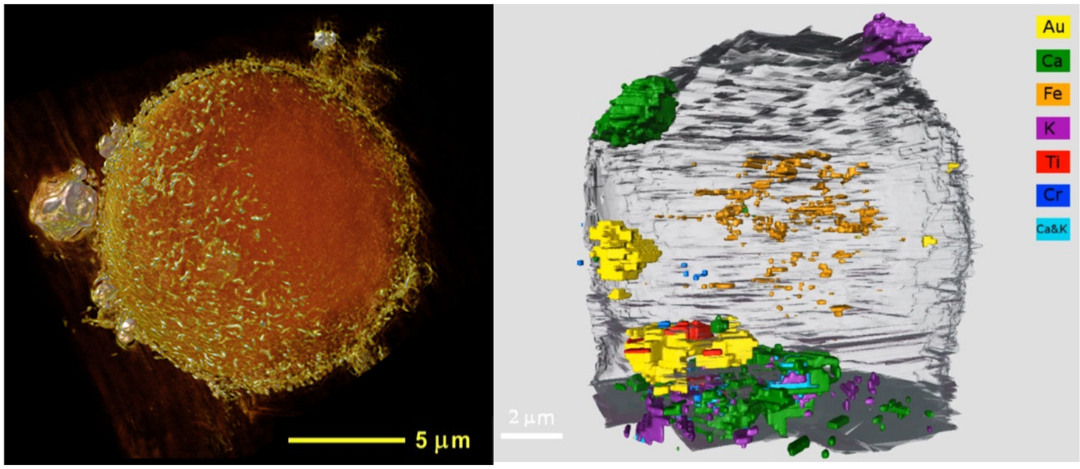

Fig. 1: Fly ash particle: *Nanotomographic reconstruction (left), and 3-D X-ray fuorescence map combined with structure (right).*

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Nanoscale Computed Tomography Reconstructions with Overlaid 3D Quantized Fluorescence

Benjamin Stripe[1], Robert Winarski[2], Lynn Trahey[3], Daniel Rosenman[2], Ralu Divan[2], Volker Rose[12]

[1]Advanced Photon Source, Argonne National Lab, 60436 Argonne, USA
[2] Center for Nanoscale Materials, Argonne National Lab, 60436 Argonne, USA
[3] Chemical Sciences and Engineering, Argonne National Lab, 60436 Argonne, USA

Nanoscale x-ray computed tomography (nCT) reconstructions offer a unique means to view structure and structural changes of solid objects on the nanoscale. The use of both x-ray absorption spectroscopy and x-ray fluorescence microscopy techniques have been used to extend nCT work to included elemental and chemical contrast. The goal of this work is to generate a three dimensional reconstruction of the object which is not only a contrast mechanism but also accurately quantifies element concentration and chemical states. To achieve this goal we have developed a method where the nCT reconstructions are used to develop 3D model elemental maps. The model is then used to compute the theoretical x-ray fluorescence microscopy map, which is then iteratively fit to the experimental x-ray fluorescence microscopy data. The end result is a three dimensional reconstruction with a quantifiable elemental concentration per voxel.

Prime examples for the power of this new technique are the study of nanoscale intermetallic compound formation in Su-Ag-Cu solder and density changes in cycled LMNCO battery cathode particles. These examples will be used to illustrate the need for future quantified spectroscopic studies, acquisition strategies, and instrumentation limitations and developments. The ultimate goal of developing methodologies and instrumentation capable of near real time, in situ, three-dimensional elemental and chemical mapping would have a enormous impact in nanoscience and nanotechnology.

P1

Growing Molecular Wires on Hydroxylated Rutile TiO_2(011) Surface

M. Kolmer[1], R. Zuzak[1], A. Zebari[1], S. Godlewski[1], J. Prauzner-Bechcicki[1], D. Bléger[2],
S. Hecht[2], M. Szymonski[1]

[1] *Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University, Reymonta 4, PL 30-059, Krakow, Poland*

[2] *Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin, Germany*

On-surface polymerization has become very attractive in many fields of nanoscience [1]. However, mainly such polymerization reactions have been shown on metal substrates [2,3]. In our previous work we have reported on covalent coupling of 10,10'-dibromo-9,9'-bianthryl (DBBA) molecules on a rutile TiO2(011) surface [4]. We have demonstrated low temperature scanning tunneling microscopy (LT-STM) data and density functional theory with the inclusion of (semi-empirical) dispersion interactions (DFT-D) calculations to prove that thermally triggered DBBA create polyanthrylene chains on a rutile surface. Also we postulate a new C-C coupling mechanism which involves proton transfer from rutile surface hydroxyl groups to the precursor molecule. The proton plays a role in weakening of a C-Br bond.

The proposed mechanism of on-surface polymerization reaction needs further experimental verification. Thus, we would like to present our LT-STM and mass spectroscopy(MS) studies on covalent coupling of diiodoterfluorene (DITF) and dibromoterfluorene (DBTF) on a rutile TiO2(011) surface (Fig 1). We show that sufficient surface reduction state is an important factor for the reaction to occur. Moreover we demonstrate that the polymerization reaction can be effectively steered by varying the number of surface hydroxyls present on TiO2(011) sample.

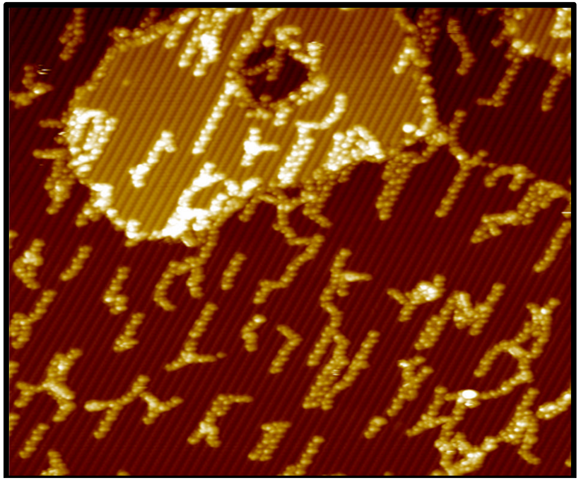

Fig. 1: *Polyfluorene chains on rutile TiO2 (011) surface*

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P2

Electrical Failure Properties of Self Assembled Cu-Si Nanowires on Si(110)

Poh-Keong Ng[1], Jian-Yih Cheng[2], Brandon Fisher[3], Carmen Lilley[1,2]

[1] *Department of Electrical and Computer Engineering, University of Illinois, 60607, Chicago, USA*
[2] *Department of Mechanical and Industrial Engineering, University of Illinois, 60607, Chicago, USA*
[3] *Center for Nanoscale Materials, Argonne National Laboratory, 60439, Lemont, USA*

Electrical failure due to current stressing is a fundamental concern in nanowire applications [1, 2]. As such, the electrical current limits of a nanowire are critical material properties needed to design a reliable electrical system. However, most current failure studies have been performed on top-down fabricated nanowires [1], which usually produces polycrystalline nanowires. Since it is expected that single crystalline nanowire will have a higher tolerance against electrical current stress, it is important to characterize the current failure of single crystalline nanowires for future applications of nanotechnology. In our studies, an electron beam evaporation method in ultrahigh vacuum was used to self assemble Cu-Si nanowires on Si(110). *In situ* failure current density measurements were performed on Cu-Si nanowires with two different test conditions: (1) failure current density versus nanowire length and (2) failure current density versus nanowire cross-sectional area. Data from the former are plotted and shown in Figure 1. A detailed overview of this work will be discussed in this presentation.

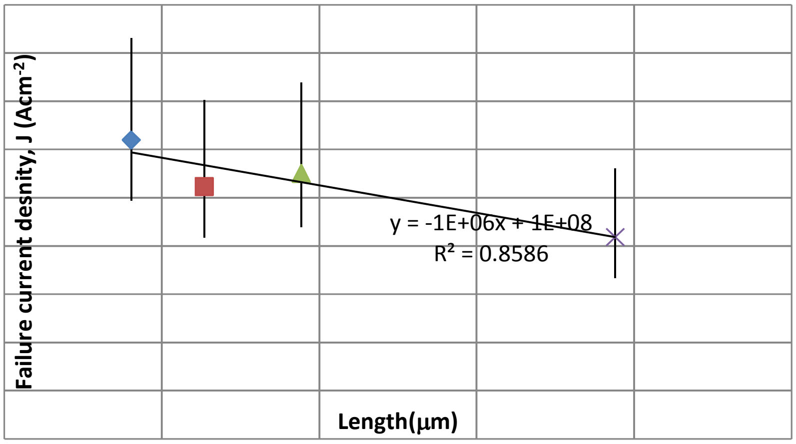

Fig. 1: *Analysis of failure current density trend with respect to the nanowire length. For this measurement, a single long Cu-Si nanowire was used. Therefore, the experiment could be repeated several times while maintaining a consistent cross-section area of the nanowire.*

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Three-dimensional Transfer of Graphene

Jonghyun Choi[1] and SungWoo Nam[1]

[1]*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Champaign, IL, USA*

Graphene has received significant attention for its potential applications such as ultrafast photodetectors and transistors, and bioelectronic interfaces, owing to its exceptionally high carrier mobility, transparency, and mechanical stability/flexibility [1-2]. Furthermore, a large elastic deformation is achievable for graphene without perturbation/degradation of the electrical properties, providing a promising platform material to realize flexible and 3-dimensional (3D) optoelectronics and bio-electronics [3]. Here, we report a novel 3D transfer method of graphene that can lead to a 3D structure of graphene for various potential applications. To carry out nonplanar 3D transfer of graphene, 3D polydimethylsiloxane (PDMS) structures were fabricated. To provide ductility that is critical for the conformal transfer/interfacing of graphene with underlying 3D substrates, a thin Au layer was used as a transfer/sacrificial material for the solution transfer process. O_2 plasma treatment of the PDMS was implemented before the transfer to facilitate the 3D conformal graphene transfer without suspensions. Vapor-phase etching of Au layer was performed in a sealed chamber to prevent the delamination of graphene during the etching process, which is challenging for the conventional wet-etching process. Raman characterization and scanning electron microscope (SEM) imaging demonstrated the graphene was successfully transferred over a broad area without significant suspensions/damages. The proposed integration procedure of free-standing graphene onto nonplanar structures will pave the way for the graphene-based 3D optoelectronics and bioelectronics in the future [4-5].

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P4

Spin-Dependent Transport through Single C_{60} Molecules

X. Fei[1,2], H.-J. Gao[2], L. Gao[1]

[1]*Department of Physics and Astronomy, California State University Northridge, 91330, Northridge, USA*
[2]*Institute of Physics, Chinese Academy of Sciences, 100190, Beijing, China*

A magnetic tunnel junction (MTJ) is composed of two ferromagnetic metal layers separated by an ultrathin tunnel barrier layer, and is the basis for many magnetoelectronic applications including the read-heads of modern hard disk drives, biosensors, microelectromechanical systems, magnetic storage element of magnetoresistive random-access memory, etc. The miniaturization of MTJs is motivated by the trend towards increasing the density of magnetic data storage and the spatial resolution of magnetic sensors. One approach for that is to use single molecule as the tunnel barrier of MTJs. Organic molecules are promising materials for next-generation spintronic devices due to the weak spin-orbit coupling and weak hyperfine interaction in organic molecules. Spintronic devices consisting of single molecules hold the promise to produce smaller, faster, and more energy efficient spintronic devices. In this presentation, we discuss the spin-dependent transport in MTJs with single C_{60} molecules as the tunnel barrier measured with a scanning tunneling microscope (STM). In the studied MTJs, one ferromagnetic electrode is the cobalt (Co) islands, showing two opposite out-of-plane magnetization directions, on the Cu(111) surface; and the other ferromagnetic electrode is a magnetic STM tip with an out-of-plane spin sensitivity. The conductance through single C_{60} molecules in the MTJ structures was measured in contact regime at 5 K. A spin-dependent conductance has been observed in our measurements.

P5

CNT-based Smart Tips for Synchrotron Assisted STM

Evgeny Nazareski[1], Marvin Cummings[2], Fernando Camilo[3], Daniel Rosenmann[2], Ming Lu[3],
Nozomi Shirato[2], Xiao Tong[3], Weihe Xu[1], Volker Rose[2], Hui Yan[1]

[1]Brookhaven National Laboratory, 2 Center Street, Upton, NY, USA
[2]Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL, USA
[3]CFN, Brookhaven National Laboratory, 2 Center Street, Upton, NY, USA

Synchrotron Assisted Scanning Tunneling Microscopy (SXSTM) is a novel technique aimed to achieve real space chemically specific imaging with atomic resolution. Chemical sensitivity of SXSTM relies on excitation of core electrons by incident X-rays when their energy is tuned to an absorption edge of a particular element. There are many contributions to the detected STM current which include those from core-level electrons (chemically specific), photoelectrons current, secondary Auger electrons current and others. It is not trivial to distinguish between various current contributions, therefore ‘smart STM tips’ have to be developed and implemented to separate chemically specific current from other constituents.

We have developed a novel approach to fabricate ‘smart tips’ utilizing carbon nanotubes (CNT). CNTs are chemically inert to oxygen and water and possess superior physical properties (stiff, better elastic properties, high aspect ratio), which makes them ideal candidates for fabrication of ‘smart tips’ and STM imaging. In this work we present the entire process of fabrication and characterization of CNT based SXSTM tips. It includes PECVD, FIB-SEM, FIB assisted PECVD techniques with subsequent STM measurements. Present work involves scientist and researchers from both Argonne National Laboratory (ANL) and Brookhaven National Laboratory (BNL).

Optical Properties of 3C-SiC Nanowires Coated by Conformal Amorphous Oxides

F. Rossi, F. Fabbri, J. S .Ponraj, M. Bosi, P. Lagonegro, M. Negri, G. Attolini, and G. Salviati

IMEM-CNR Institute, Parco Area delle Scienze 37/A, 43124 Parma, Italy

Nanosystems based on cubic (3C) Silicon Carbide are very promising for bio-oriented applications, e.g. as molecule delivery vectors and nanoelectrodes, due to their high biocompatibility. In this field, an increase the optical emission yield of the SiC-based nanostructures would open new perspectives. Significant improvements have been reported by either using porous or nano-sized structures, where the luminescence is changed by surface states or quantum confinement effects. In the present work we present a different approach to increase the optical emission efficiency by coating the nanostructures with wide band-gap oxide shell, which allows an energy transfer from the shell to the core without any modification of the emission energy.

SiC/SiOx nanowires (NWs) were grown by a chemical vapour deposition method, with carbon monoxide as precursor and iron as catalyst. The modification of the NW coating was made by chemical etching, to remove the native silicon oxide shell, and further deposition of a conformal oxide layer (Al_2O_3 or Ga_2O_3) by atomic layer deposition (ALD). The ALD growth was performed in 25 cycles, injecting separately water and metalorganic (trimethyl aluminium (TMA) or trimethyl gallium (TMG)).

The characterization of the radial NW structure and oxide thickness was made by transmission electron microscopy experiments using different techniques, as energy filtered TEM, high angle annular dark field imaging in STEM mode and EDX spectroscopy and elemental mapping. These analyses showed the core-shell NW structure, with the crystalline 3C-SiC core (diameter about 20 nm) coated by an amorphous shell, either the as-grown SiOx or the ALD-grown conformal Ga_2O_3 / Al_2O_3 layer. The ALD coating is uniform along the NW length, and its thickness ranges between 5 and 8 nm, comparable for the two oxides and similar to the SiO_2 shell thickness obtained by thermal oxidation.

The light emission properties of the NW bundles were investigated by room-temperature Cathodoluminescence (CL) spectroscopy. The standard luminescence of as-grown SiC/SiOx NWs is a broad visible emission, with the most intense blue component due to the oxide shell and a shoulder at 2.36 eV related to the 3C-SiC near-band edge (NBE) emission. The intensity of this emission increases with increasing shell thickness, indicating an enhancement due to carrier diffusion from the shell to the core, possibly promoted by the alignment between oxides and SiC bands in a type I quantum-well [1,2]. After the oxide coating change, the spectrum still shows a blue band, likely due to radiative recombination from intra-gap ALD oxide states. The SiC-NBE emission shows a comparable intensity, without any energy shift, for all the oxide layer coatings at comparable shell thickness.

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P7

Microscopic and Time-resolve Investigation of Carbonyl Porphyrin on a Copper Surface

Takuma Omiya[1,2], Heike Arnolds[2], Rasmita Raval[2], Yousoo Kim[1]

[1] *Surface and Interface Science Laboratory, RIKEN, Wako, JAPAN*
[2] *Surface Science Research Centre, University of Liverpool, Liverpool, United Kingdom*

Metal porphyrins on surfaces have been studied for catalytic reactions and biological censers. These systems possibly contain axial ligands. Understanding axial ligands of surface confined porphyrins are important to clarify the origin of adsorption enhanced catalytic activity [1] and modification of ligand induced morphological and electronic structures [2]. So far, axial ligands adsorption has been studied mainly focusing on porphyrins and only a few reports paid attention for axial ligands themselves [3].

We have studied adsorption/desorption of carbon monoxide (CO) on metal porphyrin on Cu(110) surface by means of Scanning Tunneling Microscopy (STM), Reflection Absorption InfraRed Spectroscopy (RAIRS) and Sum Frequency Generation spectroscopy (SFG). CO adsorption onto center metal of porphyrin was confirmed by STM as shown in figure 1. The bright spot (indicated by arrow) corresponds with CO-Porphyrin and dim center spots have no CO molecule because we have observed the bright spots only after CO exposure. A STM tip was positioned over the center of porphyrin, and then dosed tunneling electrons. This causes change of bright spot to the dim spot, which we assigned as CO desorption. Vibrational spectroscopies successfully resolved C-O stretch mode of CO on Cu(110) and CO on metal porphyrin. In addition, weakening of C-O bond was observed by Pump-Probe SFG, which we assigned as intermediate states of CO desorption.

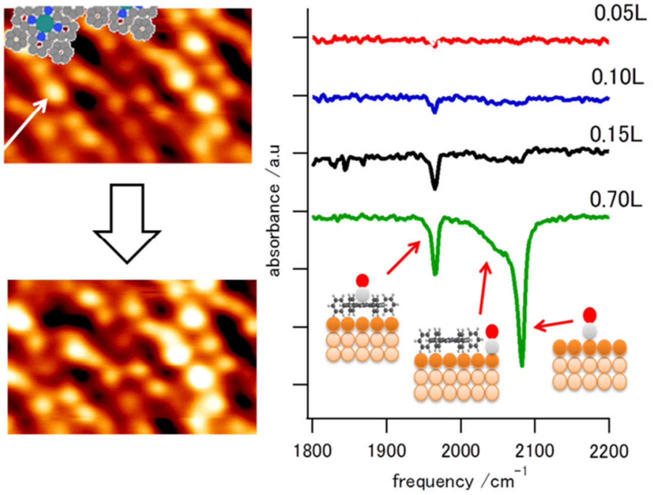

Fig. 1: *(left) STM images of CO on metal porphyrin before and after pulse injection. (right) RAIR spectra of during CO adsorption onto porphyrin layer.*

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Decoding the Ferroelectric Domains and Domain Walls Imaging Using Charge Gradient Microscopy

Sheng Tong[1], Il Woong Jung[1], Seungbum Hong[2], and Andreas Roelofs[1]

[1]Nanoscience and Technology Division, [2]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

To integrate ferroelectric (FE) materials into semiconductor devices such as FE random access memory, and tunneling devices inspires tremendous attention to understanding the local FE domain structures and dynamic behaviors. The current state-of-the-art in atomic force microscopy (AFM) modes widely used such as piezoresponse force microscopy (PFM), electrostatic force microscopy (EFM), and Kelvin probe force microscopy (KPFM) offer the spatial resolution down to a few to tens of nanometers but its unsatisfactory time resolution hinders achieving quality dynamic measurements. Recently, the emergence of a new AFM technique called charge gradient microscopy (CGM), with merits of high speed measurements to several millimeters per second, is expected to be a strong tool in dynamic imaging of surface charge distribution of polar materials, like FE domain switching and domain wall motions. It has been shown that, in CGM, the trace and retrace current polarity at the domain wall boundary are opposite and is determined by the polarization charges of FE materials, while the CGM current signals are more complex and not yet fully understood. Previous research found that high mechanical pressure applied on the probe during the CGM scans removes the surface screening charges. Thus, it is believed that the domain current signals originate from the surface charge removal and migration. To understand the surface charge migration mechanism and its contribution to the CGM signals during the CGM scan, we have patterned the surface of conductive-AFM probes *via* focused ion beam milling to isolate the current signals of domains from those of domain boundaries. As such, we establish a model of surface charge removal and interaction with the AFM probes during the CGM scans in ferroelectric domain and domain wall imaging.

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Acknowledgements

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Novel Tip Etching Method for Preparation of Scanning Tunneling Microscopy Tips with Tunable Size for Magnetic Coatings

J. Corbett , S. Pandya, A. Mandru, M. Kordesch, and A. Smith
Nanoscale and Quantum Phenomenon Institute, Department of Physics and Astronomy,Ohio University, Athens, 45701, United States of America

The development of Spin-Polarized Scanning Tunneling Microscopy (SP-STM) depends greatly on the control of the tip properties. This work conducts a systematic study with the aim of preparing idealized tips for SP-STM. Polycrystalline W wire was electrochemically etched in 2 molar NaOH at ~4.0 volts according to the ‘drop off’ method [1,2]. An addition of 0.75 ml of chemical grade acetone was added to the solution in tandem with acetone vapor saturating the W electrode-air-solution interface to control the aspect ratio, and stability of the tip. A precise amount of C-flex® tubing sheathed the W electrode to control the tension on the etching neck, and exposure to the solution, as seen in Fig 1. A secondary ~500ms pulsed polish etching was applied to reshape the apex geometry. Electron beam annealing was applied to clean the tip of contaminants and oxides. Scanning Electron Microscopy (SEM) was used to characterize the tip’s apex geometry, and it has been demonstrated that the nanoscale size of the apex is a function of the tension to a precision of less than 50 nm. Statistics on how the W electrode breaks into four distinct apex geometries is provided with current results of the second nano-scale, reshaping polish. The electron beam annealing reshapes the tip by reducing the apex size by ≤20 nm. Moreover, the method developed provides a low cost technique to manufacture W tips to varying diameter sizes that can be added to existing drop off methods. Further investigations will be to optimize magnetic coatings on different shapes and sizes of W tips. STM example images using this result will be provided for Manganese Nitride.

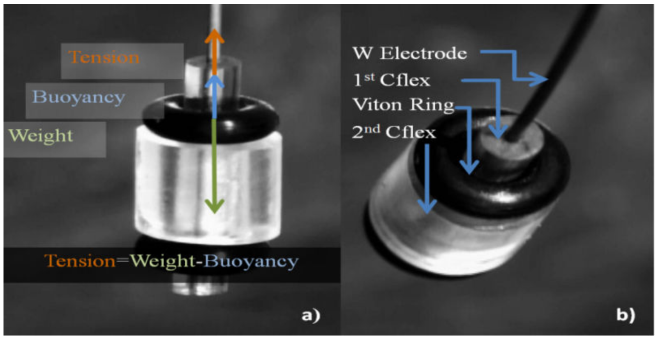

Fig. 1 *Two photographs of the bobber design. a) side view of the bobber is overlaid with a free body diagram for the tension of the etching tip. b) the image shows a downward angle of a); the blue lines indicate the design elements of the bobber and W electrode.*

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P10

Single Molecule Detection by Nanoantennas using Bi-Analyte Raman Scattering Experiments

Aftab Ahmed[1] and Reuven Gordon[2]

[1]*Center for Nanoscale Materials, Argonne National Lab. 60439, IL, USA*
[2]*Dept. of ECE, University of Victoria, Victoria BC Canada.*

Radiation patterns of optical emitters in a uniform medium are typically dipolar in nature, which is not good for collecting the emission out-of-plane. The situation can be even worse when these emitters are on a substrate, since the emission is directed into the higher-index region. Nanoantennas can be used for efficient coupling and improved directional radiation from single molecules and quantum dots.
Here we demonstrate that directional nanoantennas can offer sufficient enhancement factor to detect single molecules in Raman scattering experiments. It has been established that there is no way to count molecules by simply measuring the Raman intensities [1], therefore we have used the technique of bi-analyte Raman scattering [2] which provides convincing evidence of single molecule detection.
The ability of nanoantennas to provide sufficient enhancement for the detection of single molecule depends on local as well as far-field effects and both needs to be optimised. The feed-gap of the central dipole element must be reduced for high local fields and the radiation pattern needs to be optimised for improved excitation and by reciprocity improved collection of scattered radiation. Another important factor is the concept of impedance matching [3].

We demonstrate single molecule detection from fabricated nanoantenna with a measured feed-gap of 10 nm. The feed element is placed over a ground plane reflector at the optimum height to direct the radiation normally out of the plane of the substrate. A circular reflector around the feed element shapes the beam in the lateral plane ensuring the collection of almost all of the radiation with a numerical aperture of 0.7.
Results of Raman experiments verify the detection of single molecule, showing presence of large number of events belonging to either dye alone as compared to mixed events, which is a clear indication of single molecule Raman scattering [4].

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Development of a 4 K Laser STM for photophysical studies at the atomic scale

Haigang Zhang[1], Joseph A. Smerdon[2], Ozgun Suzer[3], Jeffrey R. Guest[1]

[1]*Argonne National Laboratory, Argonne, IL 60439, US*
[2]*University of Central Lancashire, Preston, Lancashire, UK*
[3]*San Jose Research Center, HGST, a Western Digital Company, San Jose, CA 95135, USA*

A detailed understanding of the optical and photo-physical properties of single molecules/atoms at relevant length scales is critically important for the development of molecular electronics and organic photovoltaic devices. To date, work in our laboratory has focused on electronic and structural characterization of small molecule donor and acceptor heterojunctions with variable temperature (VT) ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) and spectroscopy (STS) at 50K. In order to extend these studies to optical and photophysical properties in a stable environment, we are developing a 4 K Laser Scanning Tunneling Microscope (4K-Laser-STM) with integrated high-numerical-aperture (NA) optics behind and above the sample based on the Pan-style STM scanner. Using slip-stick inertial piezo steppers, the sample stage can be coarsely translated in X and Y directions, and, for optical experiments, a three-axis inertial lens stage can align the high-NA optics to focus laser excitation to and from photon collection at the tip-sample junction. The STM is cooled by a liquid helium bath surrounded by a liquid nitrogen jacket for operation near 4 K. Two separate ultrahigh vacuum chambers are used for sample preparation and STM measurements. We are currently nearing the end of the development phase, and hope to be commissioning the machine soon.

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P12

Edge States and Exposure to Hydrogen of Silicon at the 2D Limit on Ag(111)

Andrew J. Mannix[1,2], Brian Kiraly[1,2], Joseph Fiala[1], Mark C. Hersam[2,3], Nathan P. Guisinger[1]

[1]*Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Building 440, Argonne, IL 60439, USA*
[2]*Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, IL 60208, USA*
[3]*Department of Chemistry, Northwestern University, 2220 Campus Drive, Evanston, IL 60208, USA*

Chemical functionalization of atomically thin materials results in significant modifications to their electronic properties, which can be exploited in device applications. Compared to the chemical inertness of graphene, 2D silicon is expected to exhibit greater reactivity, and thus a greater amenability to chemical functionalization. Among potential functionalization chemistries, hydrogen termination is favored for its relative simplicity and proven efficacy with graphene and bulk Si surfaces. Using ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have studied the temperature-dependent effects of exposing 2D silicon platelets grown on Ag(111) to molecular and atomic hydrogen. At low doses, atomic hydrogen results in limited adsorption and temperature dependent etching. In the bulk, the formation of vacancies and extended etch pits is observed. Furthermore, atomic hydrogen is shown to preferentially etch domains with zigzag edges, resulting in faceted armchair edges. At high doses, atomic hydrogen completely removes silicene from the surface. These observations demonstrate the delicate balance between adsorption and etching for hydrogen exposure on silicene, informing future passivation/functionalization efforts. Moreover, the development of this edge-specific etch chemistry is useful for generating large scale edge homogeneity.

P13

Engineering of Molecular Self-Assembled Architectures using Polar Molecules

J. Neiderhousen[1,2], Y. Zhang[1], N. Koch[2], and S.-W. Hla[1,3,*]

[1]Nanoscale and Quantum Phenomena Institute, Physics & Astronomy Department, Ohio University, Athens, Ohio, 45701, USA.

[2]Institut für Physik, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 6, 12489 Berlin, Germany.

[3]Center for Nanoscale Materials, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA.

Molecular self-assembly is a fascinating process that can be used to arrange a variety of molecular networks. A vital component for controlled molecular self-assembly is understanding of how different interactions forces between the molecules play the role. Here we investigate the role of dipolar interactions between the molecules in molecular self-assembled processes of para-sexiphenyl (6P), and two fluorinated sexiphenyl isomer molecules on Ag(111) surface using low temperature scanning tunnelling microscopy in ultrahigh vacuum environment. On Ag(111) surface, the 6P forms well ordered self-assembled molecular layer with with their long molecular axis oriented to the [11-2] direction of the substrate and stack perpendicular to their long molecular axis. Interestingly, just by changing the two H atoms of the end pi-ring of 6P with two fluorine atoms, entirely different self-assemble processes are induced. We find that the dipolar interaction is favored over the hydrogen bonding in the case of fluorinated sexiphenyl isomers. The significance of van der Waals effect, dipolar interaction, electrostatic force, and hydrogen bond are also discussed in terms of how they determine molecules self-assembly.

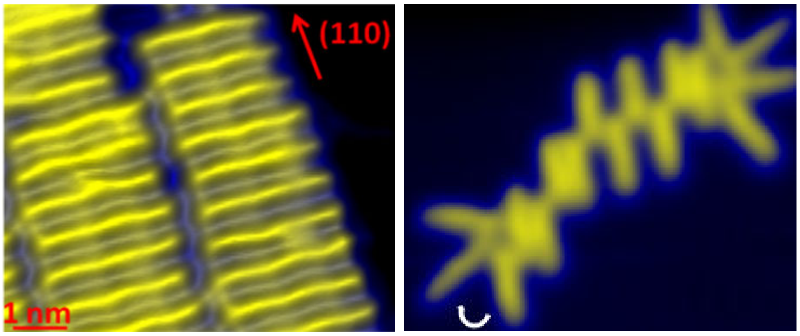

Fig. 1. 6P self-assembly (left) and fluorinated 6P assembly (right) on Ag(111).

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[Plenary] Nanoscale Studies of a 19th Century Daguerreotype Photograph

E.P. Vicenzi[1], B. Stripe[2] and V. Rose[2,3]
[1]*Museum Conservation Institute, Smithsonian Institution, Suitland, MD 20746, USA*
[2]*Advanced Photon Source, Argonne National Laboratory, Lemont, IL 60439, USA*
[3]*Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL 60439, USA*
** vicenzie@si.edu*

Summary: Nanoscale structures on the surface and near surface of daguerreotype photographs have been characterized by focused ion beam microscopy (FIB), scanning transmission electron microscopy-energy dispersive spectroscopy and nano-X-ray fluorescence spectrometry (nano-XRF). The examined features include photo contrast-inducing nanoparticles, a gilding layer, and sulfide corrosion within 19th century photographic images.

Introduction: In 1839, the daguerreotype photographic process was first presented to the scientific community in France and was widely used for roughly two decades. The current endeavor to understand the nature of the first practical form of photography, and therefore inform the long-term preservation of these objects.

Methods: Site-specific wafers were extracted from highlight regions of a daguerreotype photograph using focused ion beam microscopy. Lamellae were Pt-welded to a grid and were thinned to 70-100 nm in thickness. Hyperspectral EDS data cubes were collected in STEM mode using a Si(Li) EDS analyser and processed using multivariate statistical (MVS) algorithms designed to maximize contrast in the spatial domain [2].The hard X-ray nanoprobe at Argonne National Laboratory's Advanced Photon Source was used to collect scanning fluorescence X-ray images with a 10 keV incident beam. Focusing zone plate optics produced a 30 nm X-ray probe, rastered relative to the specimen, to collect hyperspectral nano-XRF images using a four element silicon drift EDS detection system [3,4]. Nano-XRF images and spectra are then processed using a package of software routines designed specifically for XRF data sets [5].

Results: Spatial simplicity-based MVS results reveal nanoparticle cores composed of HgAg are completely encapsulated by the Au gilding layer, instead of simply being coated on upper surfaces. Incipient Ag sulphide films are found lining voids directly beneath the photo surface and represent the earliest stages of object corrosion. Among the initial findings, fitting of the nano-XRF spectra for daguerreotype particles and gilding layers reveal Au does not make up the majority of the gilding layer. Additionally, the first quantitative analysis of an image particle reveal the composition is not entirely AgHg, but contains a significant fraction of Au.

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[Invited] Connecting Spin Waves to Charge Currents

A. Hoffmann

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

Spin waves are becoming attractive for information encoding and processing due to their long coherence lengths and times in ferromagnetic insulators with low magnetization damping. Nevertheless, in order to integrate devices based on spin waves with existing electronics it is necessary to manipulate spin waves with charge currents and voltages. One possible pathway for electric spin wave manipulation is via spin Hall effects [1], which intermix spin and charge currents. In particular, the transverse geometry of spin Hall effects is ideally suited for the integration with magnetic insulators, where the spin current can be coupled to magnetization dynamics via spin transfer torque and spin pumping. This is demonstrated in Pt/yttrium iron garnet (YIG) bilayers, where a charge current passed through the Pt layer can either reduce or increase the linewidth of ferromagnetic resonance in the YIG layer [2].

Aside from spin accumulations from spin Hall effects, another pathway for manipulating spin waves is via the Oersted magnetic fields that accompany charge currents. This can be used for guiding spin waves through curved waveguides, where otherwise the spin wave propagation is suppressed by the inherently anisotropic spin wave dispersion in thin films [3]. This same concept can be further generalized for switching spin waves between multiple waveguides [4].

Beyond manipulating spin waves with electric currents, it is also desirable to detect spin waves with electric voltages. It turns out that in metallic ferromagnets, anomalous Nernst effects enable the thermoelectric detection of spin waves [5]. Namely, the dissipation associated with the damping of spin waves, results in a local heating that for thin film structures drains into the substrate, therefore resulting in a temperature gradient perpendicular to the film plane. This in turn generates a Nernst voltage along the film, which can be detected with high signal-to-noise even far from the location of the actual spin waves. One interesting aspect of this detection scheme is that it is insensitive to the wavelength of the spin wave, and, therefore, overcomes limitations given by optical or inductive detection approaches.

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[Invited] Supramolecular Architectures at Surfaces for Probing Structure, Electron and Spin States

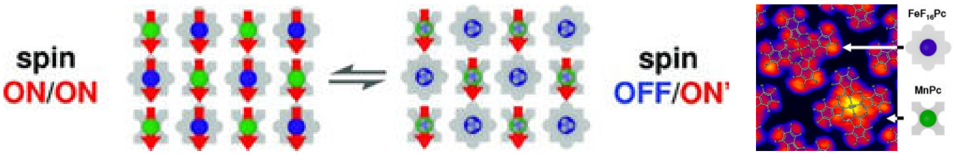
N. Ballav[1], M. Stöhr[2,7], J. Lobo-Checa[2,8], P. M. Oppeneer[3], L. H. Gade,[4] S. Decurtins, F. Diederich, C. Thilgen, A. Kleibert[1], T. A. Jung[1]

[1] *Department of Synchrotron Radiation, Paul Scherrer Institute, Switzerland*
[2] *Department of Physics, University of Basel, Switzerland*
[3]*Dept. of Physics and Astronomy, Uppsala University, Sweden*
[4]*University of Heidelberg, Germany*
[5]*Departments of Chemistry ETH Zürich, Switzerland,*
[6]*University of Bern, Switzerland*
[7]*Zernike Institute for Advanced Materials, University of Groningen, Netherlands*
[8]*Centro de Física de Materiales (CSIC-UPV/EHU),San Sebastián, Spain*
E-mail: thomas.jung@psi.ch

Well defined electronic and spintronic interfaces can be architectured by combining self-assembly and surface science. The atomically clean metal surface in the ultra-high vacuum provides a very specific environment affecting the behaviour of the ad-molecules as well as the adsorbent-adsorbate interaction. Depending on the bonding at the interface, complex electronic and magnetic interactions can occur which can be explored using spectro-microscopy correlation, in this case photoemission and X-ray photoabsorption spectroscopy (PES, XAS) and scanning tunnelling microscopy (STM).

The emergence of quantum dot states from the interaction of a porous network with the 2D (Shockley) surface state of Cu(111) exhibits sufficient residual coupling to show the onset of a band-like structure in angle resolved photoemission [1]. Selected surface-supported molecules have been shown to exhibit ferromagnetic [2] or anti-ferromagnetic [3] exchange interaction, and their spin systems have been shown to be tunable by physical parameters and / or chemical stimuli [4]. Supramolecular chemistry can be combined with on-surface coordination chemistry to reversibly switch the spin of self-assembled bi-molecular arrays [5].

All these examples have in common that the substrate-molecular interfaces are well defined by their production from atomically clean substrates and molecular building blocks. The physics and chemistry of these unprecedented systems, which are addressable by scanning probes, provide insight into novel materials in their assembly, their electronic and spintronic properties which emerge from the interaction of their components down to the scale of single atoms, molecules and bonds.



Scheme. 1. Controlling the spin state of a supra-molecular array of Fe-phthalocyanines and Mn-phthalocyanines by NH_3.

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[6] For a complete list of contributing authors refer to the individual publication.

[Invited] Live STM observation of the growth of graphene and *h*-BN

J.W.M. Frenken[1,2], D.W. van Baarle[2], G.Dong[2]

[1]*Advanced Research Center for Nano-Lithography, Amsterdam, The Netherlands*
[2]*Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands*

Chemical vapor deposition (CVD) of graphene and other monolayer materials on metal substrates establishes one of the routes towards the scalable, industrial production of these materials. However, the defect density in CVD-grown monolayers is orders of magnitude higher than that in layers obtained by exfoliation of bulk material, such as graphene flakes harvested from graphite. Defects have dramatic consequences for the properties of the CVD-grown layers, e.g. electronic and mechanical.

In search for the origins of the defects in CVD-grown graphene and *h*-BN, we have used a dedicated, variable-temperature scanning tunneling microscope (VT-STM) [1,2] in order to follow the growth of these materials on various metal substrates under the actual, high-temperature growth conditions, i.e. up to temperatures above 1000 K. This has enabled us to draw detailed conclusions about the crucial aspects of the growth mechanism [3-5]. Examples are the role of the lattice mismatch between the graphene and the metal substrate, the role of carbon dissolution and segregation, the role of atomic mobility of the metal substrate during deposition, the limited degree to which the overlayer can be improved after it has been formed, etcetera.

Based on the insights derived from these experiments, we have constructed a pilot production setup that produces single-layer, single-orientation, high-quality graphene on 2-inch diameter substrates. This process is currently being improved and professionalized by the company Applied Nanolayers BV [6].

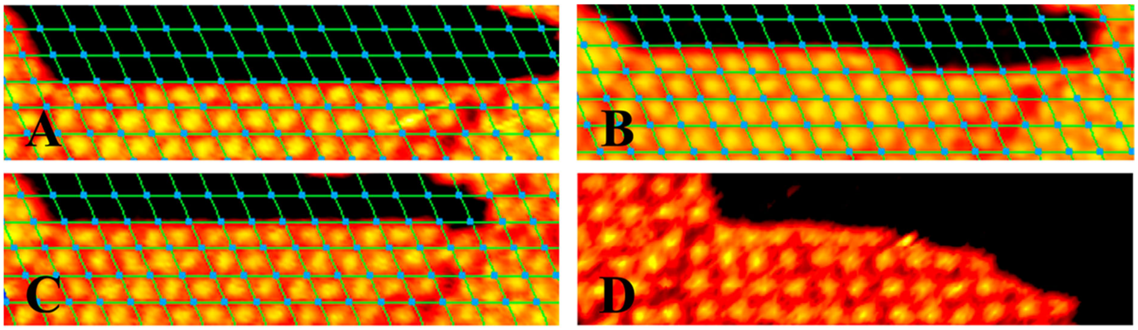

Fig. 1: *Snapshots (55 × 15 nm^2) from an STM movie during graphene growth at 975 K on graphene-seeded Rh(111) at an ethylene pressure of 5.7×10^{-9} mbar. (A-C) Consecutive images (26.2 s each) of a graphene edge, starting out straight in (A), showing a kink in (B), which has advanced to the right in (C); all changes are discretized in units of the moiré pattern. (D) Incomplete moiré unit, as we observed occasionally. The grids in images A-C indicate the moiré pattern between graphene and the substrate. From [3].*

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Solid-Source Growth and Atomic Scale Characterization of Graphene on Ag(111)

B. Kiraly[1,2], A. Mannix[1,2], M. Hersam[1], and N. Guisinger[2]

[1]*Northwestern University, 60862, Evanston, United States*
[2]*Argonne National Laboratory, 60439, Argonne, United States*

Graphene plasmonics has recently combined near field optics with the exotic properties of graphene to demonstrate remarkable optical, biochemical, and optoelectronic architectures capable of extreme light concentration and manipulation, highly efficient photoconversion, and single molecule detection. Graphene's unique electronic structure and chemical stability make it an optimal platform to interface with both light and matter; however, current devices are limited by the low-throughput or non-pristine processing steps to produce either the exfoliated or CVD transferred graphene, respectively. In this regard, it would be highly useful to grow a layer of graphene directly on top of a plasmonic metal substrate.

In this work, we report the novel growth of graphene on a bare Ag(111) single crystal. Growth was accomplished by evaporating atomic carbon onto a Ag(111) surface at elevated temperatures under ultra-high vacuum (UHV) conditions. The growth was verified and examined in-situ via scanning tunneling microscopy (STM)/scanning tunneling spectroscopy (STS) and further qualified via ex-situ Raman spectroscopy, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). While the minimal C solubility in Ag suggests similar growth behavior to other noble metals (Cu, Au), this growth mode demonstrates markedly different signatures: nanoscale dendritic features, both terrace and step nucleation, strong electronic scattering at the graphene boundaries, and highly mobile Ag adatoms interacting with the graphene growth front. Furthermore, the growth was carried out at temperatures (600°C-700°C) much lower than the temperatures commonly used for conventional chemical vapor deposition (CVD) techniques (>1000°C) and it could be extended to a variety of weakly interacting substrates, including non-metals. The all observed growth was electronically characterized as single-layer graphene, and was further supported by the narrow full-width half-maximum (FWHM) of the 2D Raman band. A 50% decrease in the Ag-O peak in the O1s spectrum reveals that the graphene layer protects the underlying silver from environmental degradation. Two predominant Moiré patterns were observed in the graphene; their periodicity was ~1.55nm and ~0.95 nm corresponding to lattice offsets of ~4.5° and ~13°, respectively. Finally, the graphene grown on Ag is weakly bound to the surface indicated by the stark contrast between the dI/dV spectra of the graphene and bare silver surface. The graphene-Ag system demonstrated in this study could immediately be applied to tip-based molecular spectroscopies and will lead to the development of more advanced hybrid graphene plasmonics.

Silicon growth at the two-dimensional limit on Ag(111)

Andrew J. Mannix[1,2*], Brian Kiraly[1,2*], Brandon L. Fisher[1],Mark C. Hersam[2,3†], Nathan P. Guisinger[1†]

[1]*Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Building 440, Argonne, IL 60439, USA*
[2]*Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, IL 60208, USA*
[3]*Department of Chemistry, Northwestern University, 2220 Campus Drive, Evanston, IL 60208, USA*

[*]Both authors contributed equally to this work

Bulk silicon has played a dominant role in the growth of microelectronics over the past 50 years. Considering the immense interest in two-dimensional (2D) materials (e.g., graphene, MoS_2, phosphorene, etc.), the growth of Si in the 2D limit is of high relevance to the evolution of electronic materials. Utilizing atomic-scale, ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have investigated the 2D limits of Si growth on Ag(111). In agreement with previous reports of *sp*^{2}-bonded silicene,[1,2] we observe the evolution of ordered 2D phases, which we attribute to apparent Ag-Si surface alloys. At sufficiently high Si coverage, we observe the precipitation of crystalline, *sp*^{3}-bonded Si(111) domains. These domains are capped with a √3 honeycomb phase that is indistinguishable from the √3 honeycomb-chained-trimer (HCT) reconstruction of Ag on Si(111).[3,4,5] Additional evidence suggests that silicon intermixing with the Ag(111) substrate is followed by the precipitation of crystalline, *sp*^{3}-bonded silicon nanosheets. These conclusions are supported by *ex-situ* atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Even at the 2D limit, scanning tunneling spectroscopy shows that the *sp*^{3}-bonded silicon nanosheets exhibit semiconducting electronic characteristics.

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[Invited] Nanofabrication of Diffractive X-ray Optics for Applications at Synchrotrons and XFELs

C. David, P. Karvinen, I. Vartiainen, I. Mohacsi
Paul Scherrer Institut, CH-5232 Villigen, Switzerland

We present recent developments in nanolithography to produce diffractive x-ray optics and we provide experimental results obtained with these devices. For the use at synchrotrons we have developed a new generation of Fresnel zone plates produced by a line doubling approach. Used in a scanning microscope, these lenses can resolve features down to 9nm in the soft x-ray range and down to 15nm in the multi keV range. To improve the efficiency for hard x-rays, a fabrication strategy was developed to produce two stacked zone plate structures on both sides of the support membrane (see Fig. 1, left). A diffraction of close to 10% was obtained at 9 keV photon energy for a zone plate with 30nm zone width. A similar technique can be applied to produce blazed zone plates with diffraction efficiencies of 50% providing 100nm spot size.

For use at x-ray free-electron laser (XFEL) sources, diffractive optics must be capable to withstand extreme radiation loads. We show how diffractive optics made of diamond can be used for various applications including nanofocusing, beam-splitting, spectral monitoring and ultrafast time resolved studies.

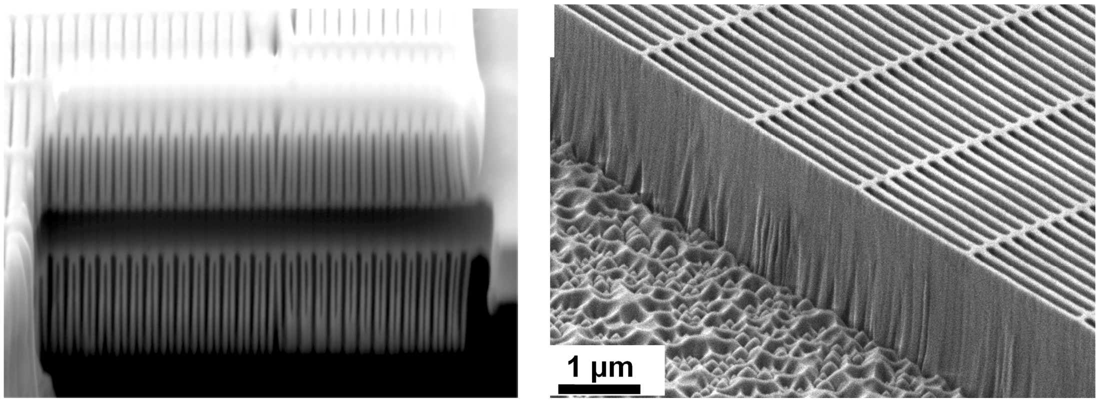

Fig. 1: Cross-section of a zone plate fabricated on both sides of the same support membrane. The resulting structures are 30nm wide and 1100nm high (left). Diamond Fresnel zone plate with for use at XFEL sources (right).

3D Electron Beam Lithography for Bio-Medical Applications

Khodr Maamari, Kasun Punchihewa, Evan Zaker, Debopam Datta, Rohit Nathani, Federico Mazza, Mattias Mengoni, Vitali Metlushko

Department of Electrical and Computer Engineering, University of Illinois at Chicago, 851 S. Morgan, Chicago, IL 60607, USA

Even though photolithography has been pushed by enhancements such as liquid immersion, phase-shift masks and optical proximity correction, the electron beam lithography (EBL) offers much better resolution. In the regular 2D EBL patterning process, an electron beam is scanned across the surface exposing the resist to break the polymer chains throughout the entire thickness of the resist down to the substrate. This creates a binary profile composed of substrate level and the resist level. Gray-scale EBL or 3D-EBL utilizes dose modulation to create a whole other state-of-the-art fabrication technique that is capable of producing sophisticated high aspect ratio 3D structures. In this more advanced technique, a dose matrix is used. With a dose matrix, different areas of the resist are exposed to varying levels of energy resulting in the break of polymer chains throughout part of the resist. Accurate 3D structures could be useful in creating integrated micro optics, such as Fresnel lenses, micro-fluidics such as “lab-on-a-chip’ or 3D scaffolds for drug discovery and tissue engineering.

Heteroepitaxial Growth of Organic Superconductors on Ag(111)

Erik Zupanic[1], Zhou Biao[2], Akira Miyazaki[3], Madoka Tokumoto[4], Igor Musevic[1], Hayao Kobayashi[2], Akiko Kobayashi[2], Abdou Hassanien[1]

[1]*Jozef Stefan Institute, 39 Jamova, 1000 Ljubljana, Slovenia*
[2]*Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan.*
[3]*Toyama University, Toyama shi, Toyama 930-8555, Japan*
[4]*AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

Nano-structured organic superconductors are novel materials to study the mechanism of unconventional superconductivity and related properties down to atomic scale limit. Of particular interest, the charge transfer complexes such as Bechgaard salt, $(BETS)_2GaCl_4$, offers a unique opportunity to probe the stability and the properties of d-wave superconductivity against competing interaction effects in a defect-free and well defined anisotropic system. In this talk, we focus on the growth mechanism of crystalline $(BETS)_2GaCl_4$ monolayer islands on Ag(111). Oriented monolayer islands of chain-like structures favor nucleation near step edges with alignment along <110> packing directions of Ag(111). This indicates a heteroepitaxial growth with BETS pairs stacking along $<\overline{11}2>$ directions. Because of lattice mismatch between $(BETS)_2GaCl_4$ and Ag(111), BETS overlapping distance is ~1Å lower than their bulk value, making it possible to alter ground state properties. High-resolution STM images show the interfacial regions, along the step edge, are aligned with <110> directions. The mechanism of Ag atoms restructuring at the step edges can be attributed to electrostatic interaction with BETS molecules that favor a clear cut alignments along <110> for interfacial stability. This type of growth may provide unique guidelines to engineer a highly oriented pattern of nanoscale organic superconductors on metal surfaces.

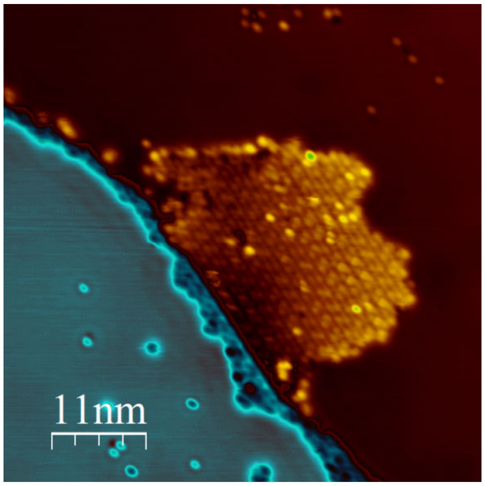

Fig. 1: A *monolayer island of organic superconductor* $(BETS)_2GaCl_4$ *grown epitaxially near step edge of Ag(111)*

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29 July 2014 Tuesday (Afternoon Sessions)

Decoding the Mystery of Additives in Organic Solar Cells

W. Chen[1,3] and S.B. Darling[2,3]

[1]*Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 USA*
[2]*Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439 USA*
[3]*Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637 USA*

Solvent additives are prevalent in today's high-performance organic photovoltaics (OPVs) [1], yet the mechanism underlying their role in improving power conversion efficiency (PCE) has remained elusive. The general picture of a correlation between solvent constituents and the morphology within the deposited active layer film is clear, but the nature of this correlation is unknown—and it must be deciphered in order to adopt a more rational approach to improving device function. Using a combination of characterization techniques including x-ray and neutron scattering as well as advanced electron microscopy, we probe the influence of additives on active layer morphology in several state-of-the-art bulk heterojunction (BHJ) blend systems. Through the integrated analysis of real- and reciprocal-space data, we uncover new insights into the role of additives that can be generalized across multiple materials.

Interactions among BHJ components, host solvent, and additives are critical for achieving proper phase-separated domains with highly efficient exciton dissociation and carrier transport. In this work, we determine the mechanisms for morphology control based on solvent additives, connecting them to a qualitative shift in the morphology formation process. This new insight into the role of additives provides a pathway for rational design of optimized morphology in OPV active layers.

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Fast Optoelectronic Spectroscopy of a Cuprous Oxide/Copper Schottky Barrier Photovoltaic Device

Laszlo Frazer[1], Kelvin B. Chang[2], Leo Ocola[3], Liliana Stan[3], Daniel Rosenmann[3], Kenneth R. Poeppelmeier[2,4], John B. Ketterson[1,5]

[1]Department of Physics and Astronomy, Northwestern University, 60208, Evanston, USA
[2]Department of Chemistry, Northwestern University, 60208, Evanston, USA
[3]Center for Nanoscal Materials, Argonne National Laboratory, 60439, Argonne, USA
[4]Chemical Sciences and Engineering Division, Argonne National Laboratory, 60439, Argonne, USA
[5]Department of Electrical Engineering and Computer Science, Northwestern University, 60208, Evanston, USA

Cuprous oxide (Cu_2O) is a direct gap (2.173 eV) semiconductor with rare structural, optical, and excitonic properties. Low cost photovoltaic and photocatylitic cuprous oxide devices are under active development. We grew large crystals of cuprous oxide using the floating zone method. Crystal growth parameters were optimized to reduce cupric oxide precipitation, copper vacancies, and strain in the crystals to improve the samples' exciton luminescence. Small cuprous oxide/copper Schottky barrier devices were fabricated using electron beam lithography. An additional, inert gold electrode was interdigitated with the copper electrode to complete the circuit.

A picosecond pulsed optical parametric amplifier tunable light source was used to illuminate the device in front cell and back cell geometries. The time resolved photocurrent was recorded at temperatures from 2 K to 300 K. In the back cell geometry, we found a prompt sub-bandgap photovoltaic effect. The pulsed photocurrent was reduced by inducing photoconductivity in the crystal using a continuous wave, above the bandgap laser.

This work was performed in part at the Center for Nanoscale Materials, a U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences User Facility under Contract No. DE-AC02-06CH11357.

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Layer-by-Layer Fabrication of Oriented Porous Thin Films Based on Porphyrin-Containing Metal-Organic Framework

Monica C. So[a], Shengye Jin[2], Ho-Jin Son[a],
Gary P. Wiederrecht[b], Omar K. Farha[a], Joseph T. Hupp[a]

[a] *Department of Chemistry, Northwestern University, Evanston, IL 60208*
[b] *Nanoscience & Technology Division, Argonne National Laboratory, Argonne, IL 60439*

Given that energy migration in natural photosynthesis is generated by highly-ordered porphyrin pigments (chlorophylls), equally highly ordered porphyrin-based metal–organic frameworks (MOFs) might exhibit similar behavior. Ideally a MOF-based strategy could facilitate antenna-like light-harvesting and position such materials for solar energy conversion. Previously, we reported that in a metalloporphyrin-based, pillared-paddlewheel type MOF, **DA-MOF**, a photo-generated exciton can migrate up to 45 porphyrin struts within its lifetime and with a high anisotropy along a preferred direction [1]. However, incorporating single crystals of **DA-MOF** into films, a structure relevant to solar energy conversion devices, is a significant challenge. Herein, we report the synthesis and characterization of two thin films of porphyrin-based MOFs on functionalized surfaces using a layer-by-layer (LbL) approach (Fig. 1) [2]. Profilometry measurements confirm that the film thickness increases systematically with number of growth cycles. Polarization excitation and fluorescence measurements indicate that the porphyrin units are preferentially oriented, while X-ray reflectivity scans point to periodic ordering. Ellipsometry measurements show that the films are highly porous. Since there are currently few methods capable of yielding microporous MOFs containing accessible free-base porphyrins, it is noteworthy that the LbL growth permits direct MOF incorporation of unmetalated porphyrins. Long-range energy transfer is demonstrated for both MOF films. The findings offer useful insights for subsequent fabrication of MOF-based solar-energy-conversion devices.

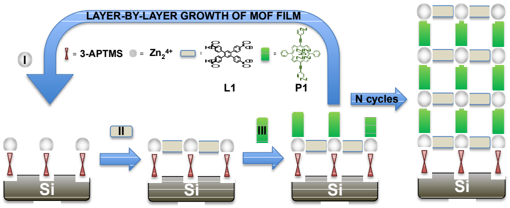

Fig. 1: *Schematic diagram for the step-by-step growth of the DA-MOF structure on idealized 3-APTMS, resulting in (b) a film after N cycles of growth.*

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Thickness Dependence of Electronic Structures of Single H_2Pc on NaCl Ultrathin Insulating films

M. Imai[1, 2], H. Imada[2], T. K. Shimizu[3], M. Kawai[1], Y. Kim[2]

[1]Department of Advanced Materials Science the University of Tokyo,
277-8561, Kashiwa, Japan
[2]Surface and Interface Science Laboratory, RIKEN, 351-0198, Wako, Japan
[3]National Institute for Materials Science, 305-0047, Tsukuba, Japan

Tuning the electronic structure of organic molecules in contact with metal substrates is essential to achieve efficient charge transport in various organic devices. Ultrathin insulating films are useful in this regard because they work as buffer layers. In addition to electronically decoupling adsorbates from metal substrates, new dimensionality, *i.e.*, thickness, enable to control surface properties such as work function[1] and chemical reactivity[2]. There have been many reports on scanning tunneling microscopy/spectroscopy (STM/STS) studies of organic molecules adsorbed on ultrathin insulating films, but correlation between film thickness and electronic structures of adsorbates has not been clarified.[3] In this study, we investigated the electronic structure of single metal-free phthalocyanine (H_2Pc), which is a p-type π-conjugated molecule[4], adsorbed on 2 and 3 monolayer (ML) ultrathin NaCl films on Au(111) using low temperature STM/STS.

Isolated H_2Pc molecules are adsorbed on both 2 ML and 3 ML NaCl islands. STM –images of H_2Pc appear to be similar for both islands, four-lobe or eight-lobe depending on bias voltages. STS spectra acquired at the center of molecule on both islands show one peak in occupied and another in unoccupied states within the energy range of -2.5 V to +2.5 V which correspond to the highest occupied molecular orbital (HOMO), and quasi-degenerated lowest unoccupied molecular orbitals (LUMO and LUMO+1), respectively. Despite the difference of work functions between 2 ML and 3 ML NaCl islands, the energy of the HOMO levels are almost the same, which can be considered as a result of the molecular level coupling with the Fermi level of the substrate. In contrast, the LUMOs and thus the rate of HOMO-LUMO gaps are different due to image charge effect and molecular level coupling with the Fermi level. Our observation suggests only the energy of LUMO can be selectively controlled with the thickness of NaCl film on the Au(111) substrate, which implies ultrathin NaCl film can control electron transport from the substrate to the molecular layer.

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[Invited] Solar-Powered Molecular Transducers: Towards Energy Sustainable Nanomachines

J. M. Cole[1,2]

[1]*Cavendish Laboratory, University of Cambridge, UK*
[2]*Argonne National Laboratory, Argonne, IL, USA*

Artificial molecular motors that convert energy into linear or rotational motion have been widely investigated as individual units within molecular machines. For the development of associated molecular architectures, light energy provides many advantages over other (chemical or electrochemical) stimuli. Molecular machinery that can function under solar light is of particular interest since this would be energetically sustainable.

However, until recently [1], the field has been lacking a controllable, reproducible, photo-induced metastable molecular transducer in the solid-state. Indeed, controllable, correlated, photo-switching materials have been coined as "the real terra nova of solid-state chemistry".[2]

This presentation presents such a materials discovery,[1] based on a series of crystalline $[Ru(SO_2)(NH_3)_4(3\text{-chloropyridine})]Y_2$ complexes (Fig. 1, left), where Y = a tosylate or chloro-tosylate anion which acts as the molecular rotor, when photo-triggered by a light-induced SO_2 photo-isomerization in the neighboring cation. Both ground-state (GS) and metastable-state (MS1 and MS2) geometries (Fig. 1; center, top) are determined, the latter using *in situ* optical-pump xray-probe diffraction. The results show that one of these SO_2 photo-isomers, MS1, acts as a photo-trigger for molecular transduction in the neighboring anion. The mechanism by which the molecular transduction occurs is evidenced (Fig 1, right).

The prospect of using nanotechnology and nanospectroscopy to tune these molecular rotors towards photo-stimulated electronic applications, as a complement to *in-situ* optical-pump xray-probe diffraction experiments, will be discussed.

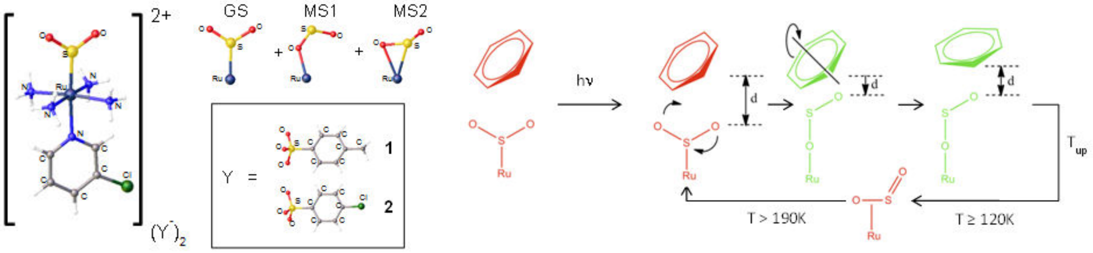

Fig. 1: *The SO_2 in the cation (left) photo-isomerizes from the ground-state (GS) to two photoisomers, MS1 and MS2 (center, top). The MS1 photoisomer acts as a phototrigger by knocking onto the phenyl ring of the counterion (center, bottom). A mechanism (right) of nanomechanical transduction between the anion and cation results to alleviate the photo-induced mechanical strain (by increasing the cation…anion separation, d); the molecular transduction is reversible by temperature tuning.*

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Entangled and Synchronized Rotation of Molecular Machines

Heath Kersell[1], Violeta Iancu[1], Yuan Zhang[1], Roman Stefak[2], Gwenael Rapenne[2], and Saw Wai Hla[1,3]

[1]*Nanoscale and Quantum Phenomena Institute, Physics & Astronomy Department, Ohio University, USA.*
[2]*CEMES, CNRS, and Université Paul Sabatier, 31062 Toulouse, France.*
[3]*Center for Nanoscale Materials, Argonne National Laboratory, 9700 S Cass Ave, Lemont, IL 60439, USA.*

Development of functional molecular devices and machines suitable to operate in solid state environments is a key goal of recent nanoscience research. Here, we investigate a multi-component molecular motor composed of a dipole active rotor arm, a Eu atomic ball bearing, and a stator units on Au(111), Cu(111), and Ag(111) surfaces using low temperature scanning tunneling microscopy (STM) and molecular manipulation techniques. The STM images reveal that individual molecular motors are rotating on Au(111) surfaces down to a substrate temperature of 7K. By using STM manipulation schemes, we are able to reposition molecular rotors on the surface into desired locations. Moreover, the rotation of the motor can be terminated by positioning a molecular block to act as a break. On Ag(111) and Cu(111) surfaces, the molecular motors form ordered self-assembled structures. We observe entangled rotation of molecular motors by increasing tunneling bias while synchronized rotation of the rotors can be induced using an electric field from the STM tip. This work is a step forward for the development of solid state compatible and responsive multi-component molecular machines. This project is financially supported by the US DOE, BES grant number: DE-FG02-02ER46012.

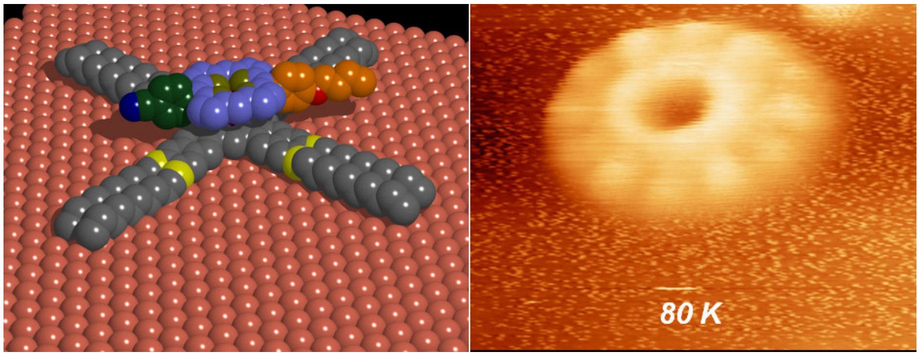

Fig. 1. A ball model of the molecular motor with dipolar rotor arms (left), and STM image of a rotating molecular motor on Au(111) at 80 K (right).

Controlled Rotation and Manipulation of Individual Molecular Motors

Y. Zhang[1], U.G.E. Perera[1], F. Ample[4], H. Kersell[1], G. Vives[2], J. Echeverria[2], M. Grisolia[2],
G. Rapenne[2,3], C. Joachim[2,4], S.-W. Hla[1]

[1] *Ohio University, Athens, OH 45701, USA.*
[2] *GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France.*
[3] *Université Paul Sabatier, UPS, 118 route de Narbonne, 31062 Toulouse, France.*
[4] *IMRE, A*STAR 3 Research Link, 117602, Singapore.*

The design of artificial molecular machines often takes inspiration from macroscopic machines, but the parallels between the two systems are frequently only superficial because most molecular machines are typically governed by quantum processes. Previously, rotary molecular motors powered by light and chemical energy have been developed. For electrically driven motors, tunneling electrons from the tip of a scanning tunneling microscope (STM) have been used to drive the rotation of a simple rotor into a single direction and to move a four-wheeled molecule across a surface. Here, we show that a single standalone molecular motor adsorbed on a gold surface can be made to rotate in a clockwise or counterclockwise direction (Fig. 1) by selective inelastic electron tunneling through different sub-units of the motor [1]. Our motor is composed of a tripodal stator for vertical positioning, a five-arm rotator for controlled rotations, and a Ru atomic ball bearing connecting the static and rotational parts. The directional rotation originates from saw-tooth-like rotational potentials, which are solely determined by the internal molecular structure and are independent of the surface adsorption site. This project is financially supported by the US DOE, BES grant number: DE-FG02-02ER46012.

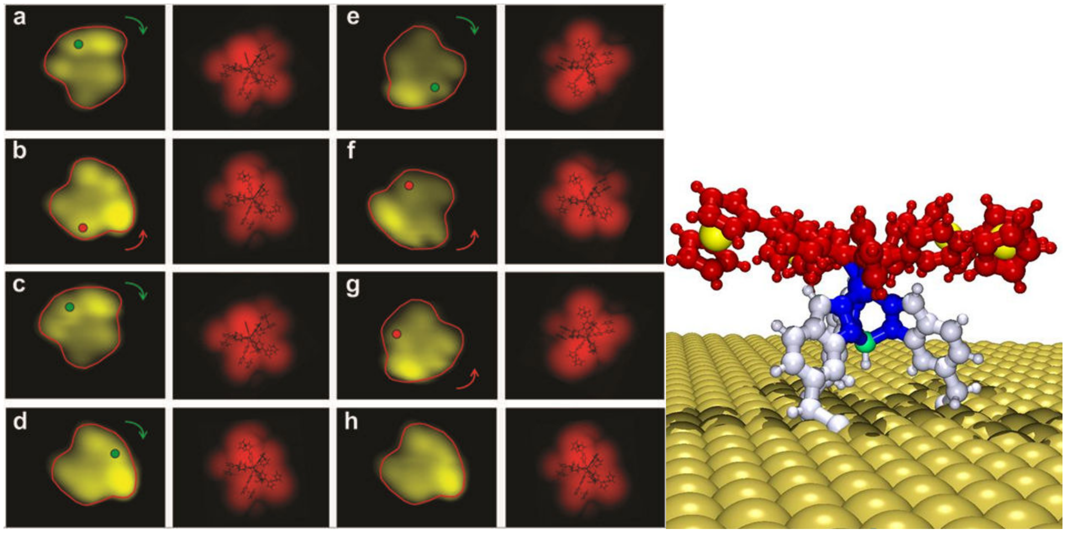

Fig. 1. Step-wise clockwise (green arrows) and counter-clockwise rotation rotation of the molecular motor (left) together with corresponding calculated structures (red). A ball model of the motor (right).

Reference

[1] U.G.E. Perera, F. Ample, H. Kersell, Y. Zhang, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, J. Joachim, & S.-W. Hla, ***Nature Nanotechnology*** 8, 46-51 (2013).

[Invited] Coherent Diffraction Imaging with Focused Hard X-ray Beams

Yukio Takahashi[1,2]

[1] Graduate School of Engineering, Osaka University, 565-0871, Osaka, Japan
[2] RIKEN SPring-8 Center, 679-5148, Hyogo, Japan

Coherent diffraction imaging with hard X-ray beams allows us to two-dimensionally or three-dimensionally observe thick objects, also providing us with unique structural information, *i.e.*, electron density distribution, not obtained by probe microscopy, or electron microscopy. We have developed high-resolution coherent diffraction imaging using the high-intensity X-ray beam focused by Kirkpatrick-Baez mirrors at SPring-8 which is the third-generation synchrotron radiation facility in Japan. For example, we visualized a three-dimensional electron density distribution of a shape-controlled Au/Ag nanoparticle[1] and Au-rich regions of individual particles of ~450 Au/Ag nanoparticles[2] at sub-10 nm resolution. Recently, X-ray free electron lasers (XFELs) become available at the SPring-8 Angstrom Compact Free Electron Laser (SACLA) in Japan. XFELs provide almost completely transverse coherent X-rays with an extremely large number of photons in a single pulse with a duration less than 100 fs. We first demonstrated the coherent diffraction imaging analysis of nanoparticles using focused hard X-ray free-electron laser pulses at SACLA, allowing us to analyze the size distribution of particles as well as the electron density projection of individual particles[3].

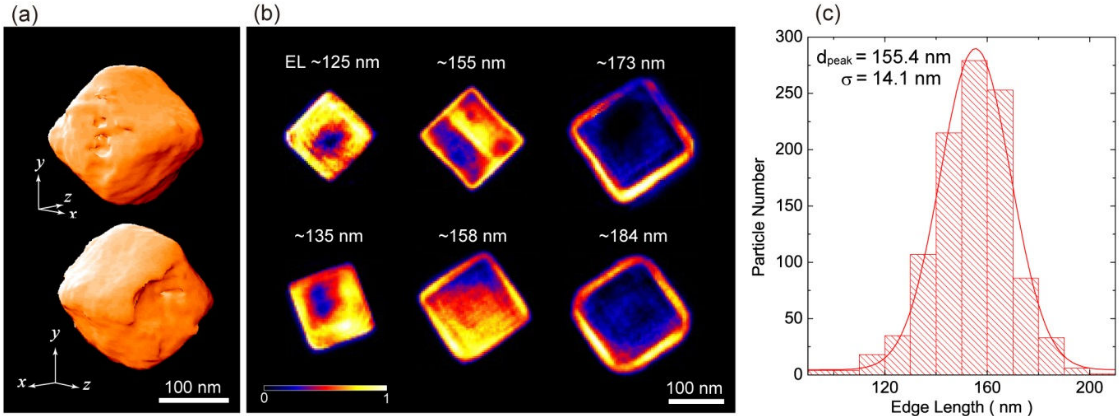

Fig. 1: (a) Isosurface rendering of a 3D reconstruction of a single Au/Ag nanobox viewed from two directions. (b) Projection images of Au/Ag nanoboxes. (c) Edge-length distribution of Au/Ag nanoboxes which were derived from speckle size of 1000 coherent diffraction patterns.

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Wide Area Distribution of Homogeneous Nanoparticles using Inert Gas Condensation Process

Sneha G. Pandya[1] and Martin E. Kordesch[1]

[1]*Ohio University, 45701, Athens, USA*

Deposition of homogeneous nanoparticles (NPs) over a large suface area is important for commercial development of various applications. Inert Gas Condensation (IGC) is used to synthesize and directly deposit homogeneous NPs over a large surface area. IGC is a technique for generating NPs where individual atoms, ions or molecules are condensed by collisions with Argon (Ar) in the plasma to form the desired particles. The plasma is produced by a radio frequency magnetron sputter gun that is placed in a chamber filled with ionized Ar gas. The NPs formed in the sputter chamber pass through a grid and are deposited on the substrate in a lower pressure chamber. Using this technique uniform diameter NPs of Copper, Zinc, Indium Nitride and Indium Antimonide were deposited over 6.45 cm^2 p-type Silicon wafers. Most of the materials that can be sputtered can be deposited in the form of NPs using this technique. The technique can be further improved to uniformly distribute these homogeneous NPs over the large surface area substrates. Moreover, it can further be expanded so that it is commercially feasible to deposit homogeneous NPs over wide area, which in turn will help in the advancement of nanoscience research for many developing fields such as Solar cells, Photodetectors, etc.

Free-Standing Nanoparticle Monolayers

Edward Barry[1], Sean P. McBride[2], Heinrich M. Jaeger[2], Xiao-Min Lin[1]

[1] *Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA*
[2] *James Franck Institute, University of Chicago, 929 E. 57th Street, Chicago, Illinois 60637*

Ligands chemically absorbed to the surface of nanoparticles (NPs) are typically used for the stabilization of NPs in their native solution against coagulation. In this talk, I will outline two features of alkane thiols absorbed to the surface of gold nanoparticles (AuNPs) that lead to robust mechanical properties and a versatile new approach of effective functionalization. First, when assembled into a monolayer, strong ligand-ligand interactions between neighboring particles render AuNP monolayers structurally rigid with a Young's modulus on the order of GPa and the ability to resist shear deformations up to 1%. AuNP monolayers of this type reproducibly cover micron-sized pores on porous substrates with remarkable stability. Second, when deposited onto a porous substrate, the ligands act as a type of molecular sieve in pressure driven filtration applications. Here, I will show how these two features enable a stable nanofiltration device and influence the transport properties of molecular dyes and proteins.

Fine Structure Splitting and Electric Field Confinement Effects of Quantum Dot Molecules

R. Thota[1], S. Ramanathan[1], G. Petersen[1], K. Wijesundara[1], M. Kerfoot[2], M. Schiebner[2], A.S. Bracker[3], D. Gammon[3], E. Stinaff[1]

[1]Ohio University, Nanoscale and Quantum Phenomena Institute, 45701, Athens, USA
[2]University of California, Merced, 95343, Merced, USA
[3]Naval Research Labs, 45555, Washington DC, USA

Semiconductor nanostructures such as Quantum Dots (QDs) are demonstrated to serve as a fundamental logic for quantum information processing. Charge carriers in Quantum Dot Molecules (QDMs) provide a mechanism to control the quantum mechanical features through the application of electric field. The samples under study consisted of a pair of $In_{1-x}Ga_xAs$ QDs separated by GaAs tunneling barrier and were grown by using molecular beam epitaxy. This work is focused on the understanding of Fine Structure Splitting (FSS) and control of the effects of molecular carrier states on the quantum confined Stark effect (QCSE) in these coupled systems. The exchange interaction between charge carriers and the anisotropy of QD during the growth formation leads to the observable fine structure splitting (FSS) of the otherwise bright states. This mixing will result in linear polarization, whose eigen states are orthogonal to each other. We used Polarization dependent Photoluminescence (PL) technique to measure the FSS as a function of electric field. We found that FSS is reduced as we tuned the electric field from highly localized state to highly molecular state. The observed FSS was on the order of 10 μev. We also present the Quantum confined Stark Effect (QCSE) results and we observed a tunable control of QCSE of excitons in these QDMs as a function of tunneling barrier [1]. The changes can be qualitatively understood by a simple model of the QDM as two coupled 1D potential wells in a field [1]. As the dots are brought together the electron and hole symmetric molecular states shift toward the midway point between the dots. Due to the difference in effective masses this will occur to differing amounts for the electron and hole resulting in a tunable QCSE as shown in **Fig. 1**.

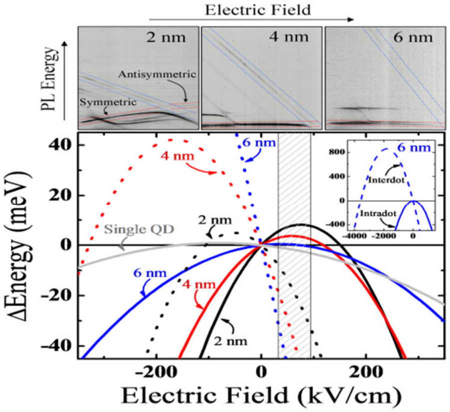

Fig. 1: *Plot of the average quadratic fits for barriers of 2, 4, and 6 nm, derived from the Stark shifts for multiple molecules measured within the shaded region, such as the representative examples shown in the top panels. With decreasing barrier, the intradot functions show an increasing concavity, or polarizability (β), and the maxima are shifting to larger positive values, indicating an increasingly positive dipole moment (p).*

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[Invited] Self-assembled donor-acceptor heterojunctions at the atomic scale: chirality, charge transfer and reversible rectification

J. A. Smerdon[1], R. B. Rankin[2], N. C. Giebink[3], J. Cho[4],
L. Gao[5], O. Suzer[6], J. P. Greeley[7], N. P. Guisinger[8], J. R. Guest[8]

[1]University of Central Lancashire, Preston, Lancashire, UK
[2]Villanova University, Villanova, PA 19085, USA
[3]Penn State University, University Park, PA 16802, USA
[4]California Institute of Technology, Pasadena, CA 91125, USA
[5]California State University, Northridge, CA 91330, USA
[6]HGST, San Jose, CA 95135, USA
[7]Purdue University, West Lafayette, IN 47907, USA
[8]Argonne National Laboratory, Argonne, IL 60439, USA

Small donor and acceptor molecules can efficiently self-assemble into heterojunctions (HJs) that are the workhorses of molecular electronics and organic photovoltaic devices. When explored in an ultrahigh vacuum (UHV) environment with scanning tunneling microscopy (STM) and spectroscopy (STS), they provide a model system in which we can untangle correlations between structure and function at the length scales critical to their behavior. We focused on pentacene (Pn, donor) and C60 (acceptor) on a Cu(111) surface. In the *in-plane* geometry, we demonstrated that these molecules can self-assemble into molecular 'pinwheel'-like HJs that are characterized by long-range order and *chirality* (see Fig.1); this is particularly surprising given the high degree of symmetry in the constituent molecules [1]. STS on the these HJs reveals small shifts in the energies of the Pn molecular orbitals that are consistent with charge transfer across the donor-acceptor interface and in agreement with density functional theory calculations (Fig. 1b). We also performed conductance measurements with the STM on *stacked* monolayer and bilayer HJs that showed electronic rectification in the predicted direction that reverses with the orientation of the HJ (Pn/C60/Cu and C60/Pn/Cu). Current efforts focus on developing these molecular systems on graphene, where we have shown through STS that the molecular states are relatively unperturbed by substrate interactions [2], and probing their optical and photophysical properties using laser excitation and light collection integrated into the UHV STM.

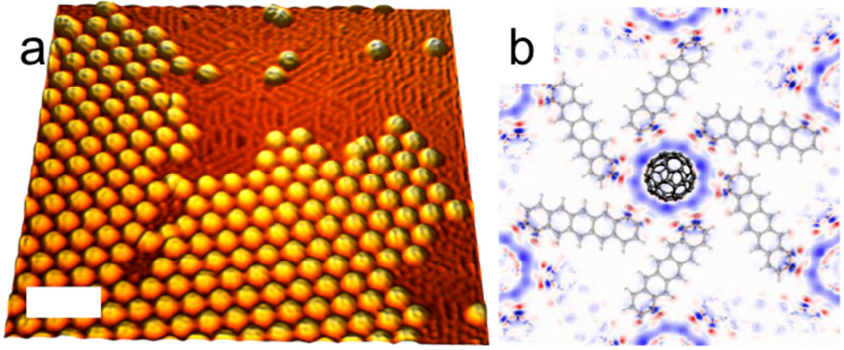

Fig. 1: *Self-assembled in-plane C60-pentacene HJs a) imaged with STM and b) modeled through DFT calculations to reveal charge transfer (blue is – and red is +, shown without Cu(111)).*

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Formation and Hydrogenation of Atomic Nitrogen on Pt(111)

Zhu Liang[1], Hyun Jin Yang[2], Junepyo Oh[2], Yousoo Kim[2], and Michael Trenary[1]

[1]Department of Chemistry, University of Illinois at Chicago, 60607, Chicago, USA
[2]Surface and Interface Science Laboratory, RIKEN, 351-0198, Wako-shi, Japan

The surface morphology and reactivity of chemisorbed N on a Pt(111) surface has been studied at the atomic level with low temperature scanning tunneling microscopy (LT-STM). A mixed NH_3–O_2 complex formed at 50 K serves as a precursor to ammonia oxydehydrogenation [1], which produces an ordered atomic N layer on the surface when annealed to temperatures above 300 K. At high coverages, two phases, $(\sqrt{3}\times\sqrt{3})R30°$-N and p(2×2)-N, are found to coexist at temperatures between 360 and 400 K. The $(\sqrt{3}\times\sqrt{3})R30°$ phase converts to the (2×2) phase as temperature increases. For both phases, nitrogen occupies fcc-hollow sites. At temperatures above 420 K, nitrogen starts to desorb. The p(2×2)-N phase shows a honey-comb structure in STM images with three nitrogen and three platinum atoms forming a six-member ring, which can be attributed to the strong binding to the underlying Pt surface. At low coverages, isolated atoms and incomplete (2×2) patches are observed [2].

After exposing the N-covered surface to hydrogen gas at 300 K, NH molecules are formed and occupy fcc-hollow sites, while H atoms occupy atop sites. Tunneling electrons from the STM tip were used to dissociate the NH bond and to induce lateral hopping of H atoms, and in both cases the responses versus applied bias voltage were measured (as shown in Fig. 1). The threshold voltages of NH dissociation and H lateral transition are found to be around 430 and 272 mV, corresponding to the excitation energy of the N-H stretching and the Pt-H stretching modes, respectively. Substitution of H by D results in an isotopic downshift of 70 and 24 mV of the threshold voltages for ND dissociation and D lateral hopping, respectively. Based on the above findings, we conclude that both processes are vibrationally induced.

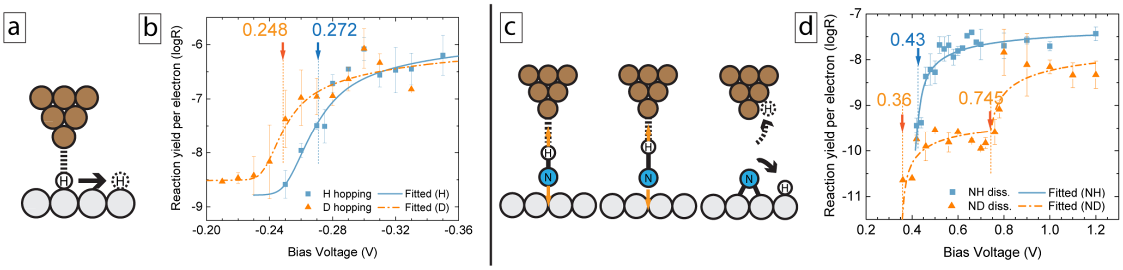

Fig. 1: *(a) Model of H hopping. Light grey circles at the bottom represent the Pt surface, while brown circles represent the tip (Tungsten in this case). (b) Action Spectra of H(blue)/D(orange) hopping. (c) Model of NH dissociation. (d) Action Spectra of NH(blue)/ND(orange) dissociation.*

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[Invited] Tracking Vacancies through Imaging, Spectroscopy and First-Principles Theory

S. J. Pennycook[1], J. Gazquez[2,3], N. Biškup[2,3], J. Salafranca[2,3], C. Cantoni[2], M. Varela[2,3],
S. T. Pantelides[4,2]

[1]*Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA*

[2]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

[3]*Departamento de Física Aplicada III, Universidad Complutense de Madrid, Spain.*

[4]*Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA*

The aberration-corrected scanning transmission electron microscope (STEM) can provide real space imaging and spectroscopy at atomic resolution with a new level of sensitivity to structure, bonding, elemental valence and even spin state. Coupled with first-principles theory, this represents an unprecedented opportunity to probe the functionality of complex nanoscale systems. A number of examples will be shown, including the microscopic origin of the barrier to O vacancy transport across grain boundaries in Y-stabilized ZrO_2, the strain stabilized generation of a spin state superlattice in $La_{0.5}Sr_{0.5}CoO_{3-x}$ (LSCO) [1], the unexpected ferromagnetism in ultrathin, insulating $LaCoO_{3-x}$ (LCO) films [2] due to a vacancy superlattice (Fig. 1), and finally, the origin of the 2D electron gas at a $LaAlO_3/SrTiO_3$ interface is shown to be not due to vacancies but to the polar nature of the substrate [3].

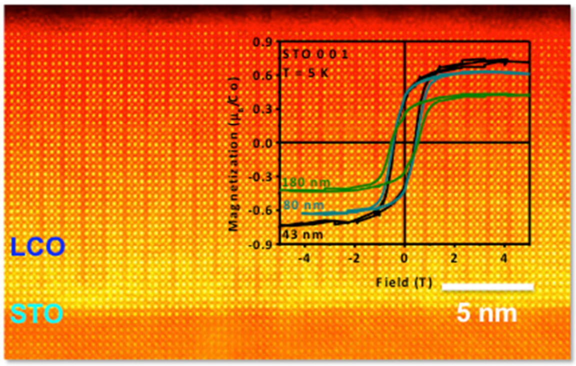

Fig. 1: *A vacancy superlattice (dark stripes) leads to insulating ferromagnetic behavior in LCO [2].*

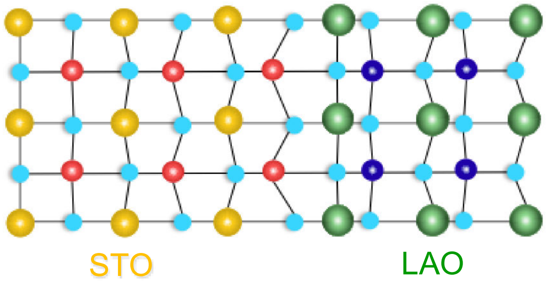

Fig. 2: *The polarization deduced by imaging and the charge distribution determined by spectroscopy are consistent with an intrinsic origin of the 2D electron gas [3].*

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30 July 2014 Wednesday (Morning Sessions)

[Plenary] Single Molecule Spectroscopy using STM

Maki Kawai[1], Yousoo Kim[2], Noriaki Takagi[1], Hiromu Ueba[3,]

[1] Department of Advanced Materials Science, The University of Tokyo, Kashiwa 277-8561, Japan
[2] *RIKEN, Wako 351-0198, Japan*
[3] *Toyama University, Japan*

Since the invention of scanning tunneling microscope (STM), spectroscopy utilizing its ultimate spatial resolution was one of the goals of the application. Not only the static spectroscopy as STS including inelastic tunneling spectroscopy but also the motion or reaction induced by the excitation of molecular states are utilized to identify the quantum states of the materials. Vibrational spectrum of a single molecule provides useful information not only for the chemical identification of the molecule [1] but also for investigating how molecular vibrations can couple with the relevant dynamical processes [2-6], where the response of vibrationally mediated molecular motion to applied bias voltage, namely an “action spectrum”, can reveal vibrational modes that are excited through STM inelastic tunneling processes, because the molecular motion is induced only *via* the inelastic tunneling processes [3-5]. The term “Action spectrum” has been known as a technique in biology and/or electro-chemistry fields to identify the specific molecule that is active in reaction induced by photons in UV-Vis region. Here with the help of theory, details of the molecular motions coupling to the vibrational excitation is unveiled.

Depending on the strength of the coupling between the molecule and substrate, spin state of the molecule changes. With strong coupling with Cu(110) the spin of FePc is completely killed whereas if decoupled as on Cu(110) 2x1-O, spin survives with change in the direction of easy axis [7]. On Au weak coupling leads to appearance of Kondo state, where a competition between the RKKY interaction affects the spin state [8]. Kondo state of FePc on Au depends on the adsorption site, where the difference was originating from the coupling with the substrate electrons [9].

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[Invited] Assembling and Probing Quantum Structures on a Semiconductor Surface by Cryogenic STM

Stefan Fölsch

Paul Drude Institute for Solid State Electronics, Hausvogteiplatz 5-7, 10117 Berlin, Germany

Scanning tunneling microscopy (STM) at cryogenic temperatures opens up the unique possibility to place individual atoms at selected positions at a surface. We applied this technique to III-V semiconductors and found that native adatoms can be repositioned by vertical manipulation [1,2], allowing us to create functional structures with atomic-scale precision. On the InAs(111)A surface, donorlike In adatoms can be positioned one at a time to form linear chains (Fig. 1). The positive charge state of these adatoms has several interesting consequences. It can be exploited, for example, to engineer multistable systems by coupling binary atomic switches via electrostatic interaction [3]. In addition, we found that a In adatom chain on InAs(111)A acts as an atomically precise quantum dot that confines surface state electrons. This enables to strictly control and tune the quantum mechanical coupling in quantum dot assemblies ('quantum dot molecules') constructed with effectively zero error.

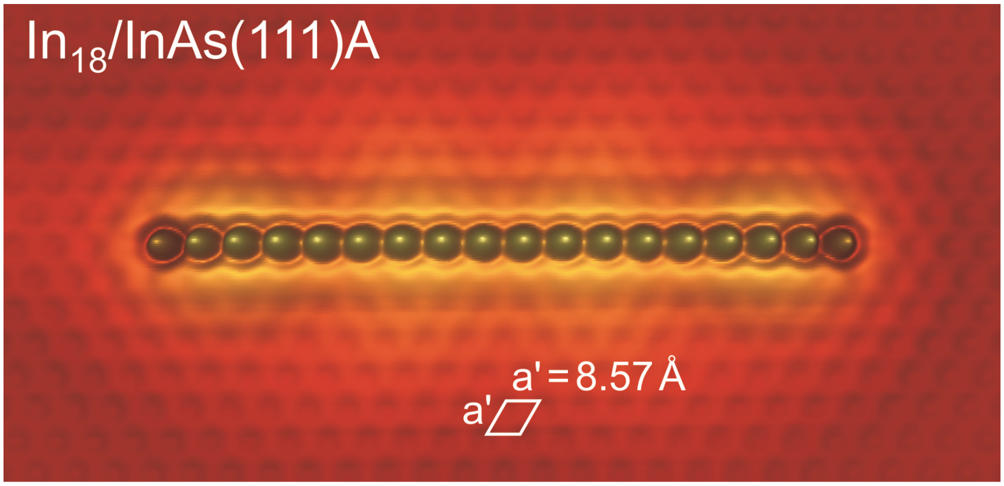

Fig. 1: *3D-rendered STM topography image (216 Å × 105 Å, 0.1 nA, 0.1 V) of a* In_{18} *chain assembled from In adatoms on InAs(111)A by vertical atom manipulation at 5 K. The chain atoms reside on nearest-neighbor In-vacancy sites of the 2×2 reconstructed surface separated by a' = 8.57 Å. The increased apparent height around the chain (displayed in light orange in the color-coded image) is due to the screened electrostatic potential induced by the positively charged In adatoms.*

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Joule-Thomson Scanning Probe Microscope for in-situ analysis in extreme environments

V. Simic-Milosevic[1]

[1] *SPECS Surface Nano Analysis GmbH, 13355 Berlin, Germany*

Due to miniaturization of modern devices down to the nanoscale the importance of knowledge and control of surface properties at this level is continuously increasing and necessary for the correct device operation. Often such devices are working at elevated or near ambient pressures of defined working gas mixtures, in liquid media, or electric potentials or magnetic fields have to be applied. Also extremely low or high temperatures might be necessary.

To contribute to advanced materials analysis and development in future means using scanning probe microscopy (SPM) and related techniques in highly demanding requirements as a key tool for nanotechnology. In UHV applications strong emphasis lies on the spectroscopic methods such as scanning tunneling spectroscopy and inelastic tunneling spectroscopy as well as single atom and molecule manipulation. For this kind of applications a system operating sample and sensors in thermal equilibrium at 1K and magnetic field up to 3T is a huge advantage over standard SPM instruments which do not work under these extreme environments. With the new Joule-Thomson SPM [1] working at 1K the thermal broadening of the Fermi edge is reduced significantly compared with what is typically observed at 4 K. As a result the resolution in spectroscopic measurements is increased significantly. The modular design allows for various experimental configurations and for the usage of different sensors as well as of the high magnetic field.

This work summarizes and presents existing solutions based on a combination of the Joule-Thomson cooling stage with extremely stable SPM heads. Future development routes to new instruments for materials analysis being functional under extreme working conditions, opportunities and limits will be discussed. Finally applications and examples will be presented.

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Manipulating Charge States of Metal-Semiconductor Interfaces

Tae-Hwan Kim[1,2], Han Woong Yeom[1,2]

[1]*Department of Physics, Pohang University of Science and Technology, 790-784, Pohang, Republic of Korea*
[2]*Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science, 790-784, Pohang, Republic of Korea*

Metal-semiconductor interfaces have drawn a lot of interest in the field of semiconductor surface and interface science, and have been one of the most essential parts in semiconductor electronic and optoelectronic devices. For example, the Schottky-barrier height experimentally observed at the metal-semiconductor interface appears to be nearly independent of the work function of the metal. Since the time of Bardeen, interface gap states seem to have been a primary mechanism of the Schottky-barrier height causing Fermi level pinning at metal-semiconductor interfaces. Recently, polarized chemical bonds at metal-semiconductor interfaces have been recognized to lead to the apparent Fermi level pinning effect. When these interface bonds are formed underneath thin metal islands grown on a silicon substrate, a spontaneous charge transfer across the semiconductor-metal interfaces occurs as a result of the difference in the Fermi level positions between the metal and the semiconductor. These polarized chemical bonds can form a dipole layer. This dipole layer can play an important role in many areas of technology, for instance, in organic light emitting diodes. However, some of the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact are yet not explored in any real detail.

In this work, we report the use of scanning tunneling microscopy (STM) to form a double-barrier tunneling junction (DBTJ) with thin metallic nanoislands grown on Si(111) and to control charges of the interface dipole layer formed between the metallic nanoislands and the Si(111) substrate. Reversible hysteric switching in their I−V and differential conductance spectra are observed due to the charging and discharging of the interface dipole layer in a similar fashion to molecular DBTJs. STM images clearly visualize the distinct charge states and scanning tunneling spectroscopy (STS) spectra reveal that quantum well states (QWSs) of the ultrathin islands act as the charging/discharging channels in analogy to the molecular orbitals in the case of the molecular DBTJs. This work demonstrates that the charges of the interface dipole layer at the nanoscale Schottky contact can be controlled by the electron transfer via the QWSs of the metallic islands.

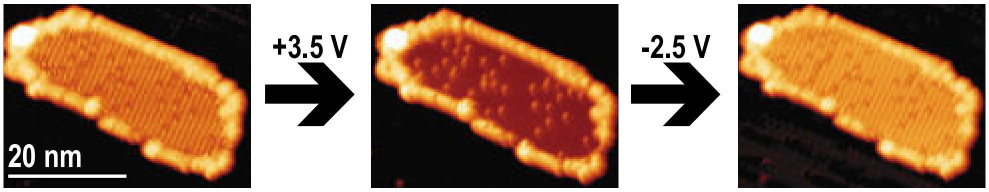

Fig. 1: *Sequential STM images show apparent height change of indium islands after charging (discharging) the interface state by applying a positive (negative) voltage pulse.*

[Invited] Scanning Tunneling Microscopy and Spectroscopy Studies of Graphene in the Quantum Hall Regime

Adina Luican-Mayer[1], Eva Y. Andrei[2], Saw Wai Hla[1]

[1] *Center for Nanoscale Materials, ANL, Argonne, IL 60439, USA*
[2]*Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08855, USA*

Seeking to understand the unique nature of the charge carriers in graphene, we performed scanning tunneling microscopy (STM) and spectroscopy (STS) experiments at low temperatures and in magnetic field. These techniques give access, down to atomic scales, to structural information as well as to the density of states. In the first part of the talk, I will discuss experimental results studying twisted graphene layers away from the equilibrium Bernal stacking which leads to the formation of Moiré patterns. Our experiments demonstrate the effect of such rotations on the electronic properties as a function of twist angle [1]. In the second part, I will present STM/STS studies of Landau quantization and its dependence on charge carrier density. Measurements were carried out on exfoliated graphene samples deposited on SiO_2, which allowed tuning the carrier density through the Si back-gate. Furthermore, by performing spatially resolved STS/STM we demonstrate the true discrete quantum mechanical electronic spectrum within the Landau level band near an impurity in graphene in the quantum Hall regime [2]. Lastly, I will discuss our recent progress in fabricating and characterizing stacks of atomically thin Van der Waals materials, in particular the charge density wave system, 1T-TaS_2.

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Graphene Silicon Interfaces at the Two-Dimensional Limit

B. Kiraly[1,2], A. Mannix[1,2], M. Hersam[1], and N. Guisinger[2]

[1] *Northwestern University, 60862, Evanston, United States*
[2] *Argonne National Laboratory, 60439, Argonne, United States*

Artificial van der Waals heterostructures have demonstrated both significant improvements of graphene's intrinsic properties and entirely new properties of their own[1]. Early interest in these structures was based on nearly ideal carrier mobility in graphene on two-dimensional (2D) hexagonal boron nitride[2]. Although exfoliation and reassembly of bulk vdW solids has yielded an impressive list of new systems, this method inherently limits the geometry and constituent materials of these structures. Growth of 2D heterostructures has been demonstrated, but mainly limited to the prototypical graphene/hBN system[3]. Adding new constituent materials, particularly those with electronic heterogeneity, to these 2D heterostructures allows them to be engineered with a variety of new properties.

We present the growth and characterization of interfaces between an atomically thin silicon layer and graphene. First, graphene is grown on Ag(111) via atomic carbon deposition at temperatures from 600°C -700°C. Following the growth of graphene, atomic silicon is evaporated on the graphene-covered Ag(111) substrate at 320°C-360°C. The resulting silicon growth results in facetted domains capped with a honeycomb lattice with periodicity 6.4 Å; Raman spectroscopy reveals peaks at 520 cm^{-1} and 900-1000 cm^{-1} that coincide precisely with bulk diamond cubic silicon, indicating these domains are comprised of sp^3 bonded crystalline Si. These 2D sheets of silicon demonstrate both semiconducting character and a honeycomb lattice is attributed to a silver-based reconstruction of the Si(111) surface. The resulting silicon domains grow in two different configurations with respect to the dendritic graphene: (1) silicon domains appear to grow directly on the Ag(111) surface and terminate at the graphene boundaries. These in-plane interfaces are atomically-precise and clearly resolved via scanning tunneling microscopy. Electronically, the density of states of both isolated constituent materials persist to these interfaces within the resolution of the measurement, indicating little interaction at the border. (2) The silicon growth is observed *underneath* the existing graphene flakes. The vertically stacked silicon graphene domains are identified via atomically resolved imaging *through* the graphene domains at larger biases where graphene is transparent under STM. Furthermore, the vertical materials interfaces demonstrate distinct electronic signatures from either constituent material. The resulting interfaces represent atomically pristine interfaces between graphene and a sp^3 bonded semiconducting Si film, demonstrating a significant step forward in the diversification of van der Waals heterostructures.

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Modeling of Photo-induced Transport in Two-Dimensional Semiconductors

E. J. Lenferink[1], Y. Jia[1], G. Wei[2], N. P. Stern[1,2]

[1]*Department of Physics and Astronomy, Northwestern University, 60208, Evanston, USA*
[2]*Applied Physics Program, Northwestern University, Evanston, 60208, USA*

When the thickness of transition metal dichalcogenides (TMDCs) such as monolayer molybdenum disulphide (MoS_2) is reduced to a sub-nanometer length scale, the symmetries of the crystal lead to two degenerate valleys that can be spectrally distinguished by circular polarization. Due to a spin- and valley-dependence of the Berry curvature [1], the transverse motion of low-energy charge carriers is coupled to their spin and valley numbers in electrically-biased monolayer TMDCs. To study valley-polarized transport and the emergence of spin and valley Hall effects in monolayer TMDCs, we have developed a formalism based on the drift diffusion model of electronic transport, recombination, and relaxation that incorporates spin and valley indices. Comparisons between numerical modeling and experimental measurements of the MoS_2 photoresponse help illuminate free carrier photogeneration and motion in nanometer-thick electrical devices under illumination.

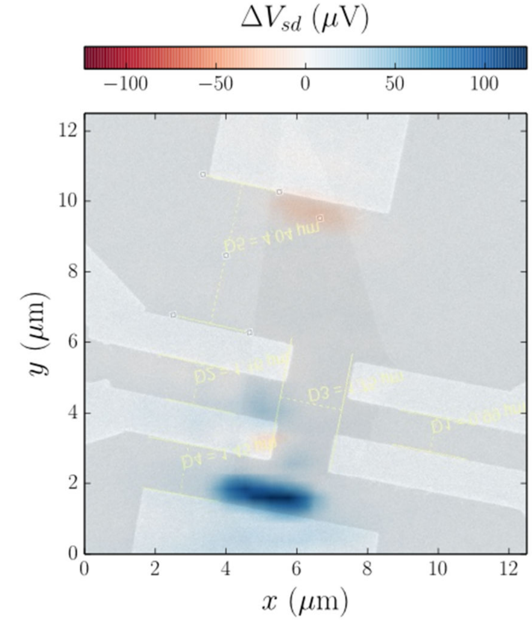

Fig. 1: *Spatial map of the photovoltaic effect in a six-terminal monolayer molybdenum disulphide opto-electronic device measured between source and drain contacts and excited by a focused laser.*

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Dangling Bond Dimer on Ge(001):H Surface: Prototypical System for Atomic and Molecular Switching

S. Godlewski[1], M. Kolmer[1], H. Kawai[2], R. Zuzak[1], B. Such[1], J. Lis[1], M. Saeys[2,3], P. de Mendoza[5], A. M. Echavarren[5], C. Joachim[2,4], M. Szymonski[1]

[1]Department of Physics of Nanostructures and Nanotechnology, Institute of Physics, Jagiellonian University, Reymonta 4, PL 30-059, Krakow, Poland
[2]Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore
[3]Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore
[4]Nanosciences Group & MANA Satellite, CEMES-CNRS, 29 rue Jeanne Marvig, F-31055 Toulouse, France
[5]Institute of Chemical Research of Catalonia (ICIQ), Avenida Països Catalans 16, 43007 Tarragona, Spain

Hydrogen passivated semiconductor surfaces, i.e. Si(001):H or Ge(001):H, are promising platforms for monomolecular electronics. As it has been shown recently, a monolayer of hydrogen atoms may decouple molecular states from semiconductor surface [1,2]. Furthermore, on the passivated semiconductor it is possible to construct dangling-bond (DB) atomic-scale structures by scanning tunneling microscope (STM) tip-induced hydrogen desorption [3,4]. Such DB wires and circuits may then serve as interconnects in molecule-based electronic devices.

The presentation will be devoted to the model system: DB dimer on Ge(001):H surface, i.e. a structure of two bonded surface Ge atoms with an unsaturated bond each. Equilibrium geometry of DB dimer is buckled, what makes it possible to switch between two energetically equivalent configurations. The oscillations of DB dimer induced in STM experiment were characterized at 4.5 K (liquid helium) temperature. Two different switching mechanisms, related to weak and strong electron-phonon coupling, will be discussed.

In the presentation we will also describe the role of DB dimer in STM imaging of prototypical, planar 3-input trinaphthylene molecules (Y molecules). It will be shown that the ground electronic state of the molecules physisorbed on Ge(001:H) surface could be accessed by STM measurement only if the molecule - substrate coupling is enhanced by surface DBs [2]. Finally we will present that Y molecules could be effectively manipulated laterally by the STM tip, as well as reversibly attached and detached from the surface DB dimers. It will be also demonstrated that attachment of Y molecule to DB dimer could promote molecule switching, what can be considered as a molecular latch operated by STM. Reversibility of the manipulation processes gives perspectives for practical implementations as molecular switches.

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Lateral motion of CO on Ag(110) surface via vibrational excitation by tunneling electron

Junepyo Oh[1], Hyunseob Lim[1,2], Jaehoon Jung[1], Yousoo Kim[1,*]

[1] *Surface and Interface Science Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198 Japan*

[2](current affiliation)*, IBS Center for Multidimensional Carbon Materials Room 302, Advanced Material Research Bldg.(103), UNIST, 50, UNIST-gil, Eonyang-eup, Ulju-gun, Ulsan*

Inelastic electron tunneling (IET) process is used not only to detect the vibrational mode of adsorbates but also to induce motion and reaction of a single molecule at metal surfaces through the vibrational excitation. The inelastic electron tunneling spectroscopy (STM-IETS) is most widely used method to detect vibrational features from the individual molecule by using IET process [1]. Although STM-IETS is a powerful tool for chemical identification of individual molecules, it cannot be applied to molecules that move or react during STM-IETS measurement, such as the dissociation of O_2 and hopping of CO induced by vibrational excitation [2,3]. W. Ho et al. have been successfully measured hindered rotation and internal stretching (IS) vibrational mode of CO on copper surfaces by using STM-IETS [4]. However, they couldn't measure the internal stretching mode of CO on Ag(110) surface. They described that the CO is well move when it is scanned at 0.25 eV, making it difficult to probe the C-O stretching mode by STM-IETS [5]. As new method of vibrational mode detection from such molecules, Sainoo et al. has been suggested action spectroscopy with the STM (STM-AS) [6]. In STM-AS method, vibrational modes to cause molecular dynamics can be assigned by measuring the molecular dynamics against applied bias voltage.

In this work, we have investigated the lateral hopping phenomena of CO molecule adsorbed on Ag(110) surface by using STM-AS method, and have successfully detected a vibrational mode related to the hopping motion for the first time [7]. The probability shows sudden increases at 64, 96, and 160 meV even though there are no vibrational modes correspond to these energies. Interestingly, however, the energy spacing between the each threshold is very closing to vibrational energy of the metal-CO molecule stretching mode (ν(M-CO), ~32 meV). We also found from the results of tunneling current (I_t) dependence of CO hopping rate that hopping motion of CO took place through multiple excitations process below 170 meV. From these results, we conclude that the origin of hopping motion of CO on Ag(110) is a overtone excitation of M-CO stretching mode. The detail of hopping mechanism will be discussed in the presentation.

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Incorporation of Metal-Organic Molecules into Artificial Nano-Cavities in Metal Surfaces by STM Manipulations

A.DiLullo[1], Y. Li[1,2], B. Fisher[1], S.-W. Hla[1,2]

[1]*Argonne National Laboratory, Argonne, IL, USA*
[2]*Ohio University, Athens, OH, USA*

We create single polyatomic vacancies on a Au(111) surface by controlled ramps of probe-sample bias and probe-sample separation. The electronic structure of these 'holes' in our surfaces are investigated by tunneling spectroscopy and analysis of field emission resonances. Metal-organic molecules, TBrPP-Co, are introduced into these surface vacancies by lateral probe manipulations from adsorption sites on the metal terraces. The electronic structure of the resulting molecule-vacancy complexes are examined by differential conductance spectroscopy and real-space mapping of field emission resonances. The measured local electron energy state densities exhibited shifts in the complex from levels observed in vacancies and TBrPP-Co molecules when separate. The studies to be presented utilize a recently commissioned low-temperature STM in the Center for Nanoscale Materials at Argonne National Laboratory.

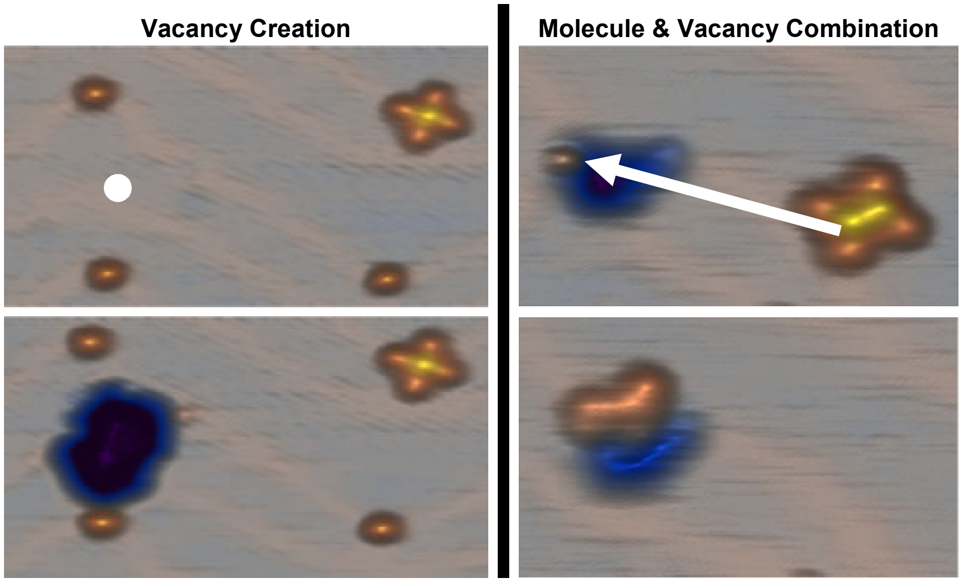

Fig. 1: *(left) Scanning tunneling microscope topographic images illustrating the result of surface vacancy creation on a Au(111) single crystal with adsorbed TBrPP-Co molecules. (right) Before and after topographic images of the Au(111) crystal after laterally manipulating a TBrPP-Co molecule into a surface vacancy.*

Lateral switching of a CO by vibrational excitation

H. J. Yang[1,2], M. Kawai[2], Y. Kim[1]

[1]*RIKEN, 351-0198 Wako, Japan*
[2]*The University of Tokyo, 277-8651 Kashiwa, Japan*

Inelastic electron tunneling (IET) process at an isolated molecule confined in the tunnel junction of a scanning tunneling microscope (STM) provides an effective pathway to excite molecular vibration leading to a variety of dynamic behaviors of the target molecule, such as lateral hopping, rotation, desorption and even chemical reaction.

Here we demonstrate a novel type of vibrationally-induced lateral switching of a CO molecule in a local c(4x2)-CO structure on the Pt(111)[1], which is clearly different from the lateral hopping of a CO on Pd(110)[2] or switching of a molecular rotor[3]. It is well known that CO on Pt(111) has two available adsorption sites, ontop and bridge sites, which reveal different adsorption energy and vibrational properties such as mode frequency and coupling, with respect to the adsorption site. We reported that the overlayer structures according to the surface coverage, focusing on the appearance of bridge CO at the center of c(4×2) unit and the contribution of bridge CO to the intermolecular interaction[4]. The bridge CO shows a bridge-to-top (b-t) switching inside the c(4×2) unit, and quantified action spectrum [5] of the b-t transition by scanning tunneling microscopy. While ontop CO never changes its position by vibrational excitation with tunneling electrons, bridge CO hops to adjacent ontop position by injecting tunneling electrons at a certain bias voltage corresponding to the CO internal stretch mode. Moreover, energy applied to an ontop CO triggers b-t switching of adjacent bridge CO molecules, implying the ontop-bridge inter-adsorbate interaction. The expected potential energy surface, mechanism of b-t hopping, and the contribution of inter-adsorbate to the lateral switching will be discussed.

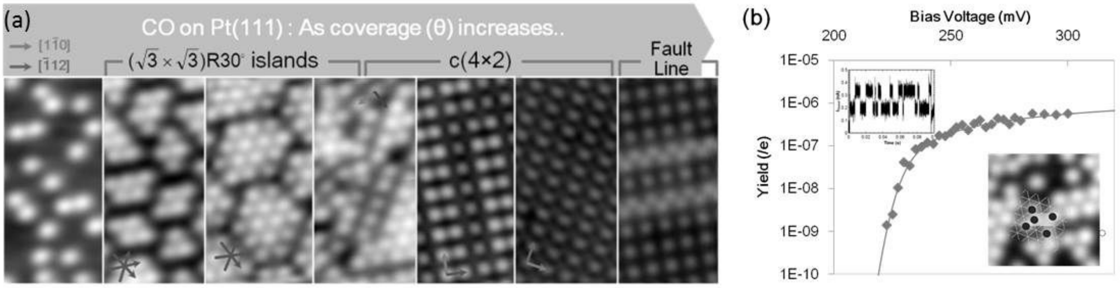

Fig. 1: (a) *STM images revealing the evolution of superstructures of CO on Pt(111) according to surface coverage.* (b) *An action spectrum and a current trace for CO switching in a local c(4x2) unit. Inset: an STM image showing CO switching.*

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[Invited] Charge gradient microscopy: high-speed visualization of polarization charges using a nanoscale probe

Seungbum Hong[a,b,1], Sheng Tong[b], Woon Ik Park[a,b], Yoshiomi Hiranaga[c], Yasuo Cho[c], and Andreas Roelofs[b,1]

[a]Materials Science Division and [b]Nanoscience and Technology Division,
Argonne National Laboratory, Lemont, IL 60439, USA
[c]Research Institute of Electrical Communication, Tohoku University, Sendai 980-8577, Japan

Polarization charges of ferroelectric materials are screened by equal amount of surface charges with opposite polarity in ambient condition. Here we show that scraping, collecting and quantifying the surface screen charges reveals the underlying polarization domain structure at high speed, a technique we call Charge Gradient Microscopy (CGM).[1] We collected the current from the grounded CGM probe while scanning a periodically poled lithium niobate (PPLN) single crystal and single crystal $LiTaO_3$ thin film on Cr electrode. We observed current signals at the domains and domain walls originating from the displacement current and the relocation or removal of surface charges, which enabled us to visualize the ferroelectric domains at a scan frequency above 78 Hz over 10 μm. The scraped charge, measured as a current that scales with scraping rate, induces a charge gradient that leads to the immediate relocation or refill of the screen charges from the vicinity of the probe. As such, we envision that CGM can be used in high-speed ferroelectric domain imaging and piezoelectric energy harvesting devices.

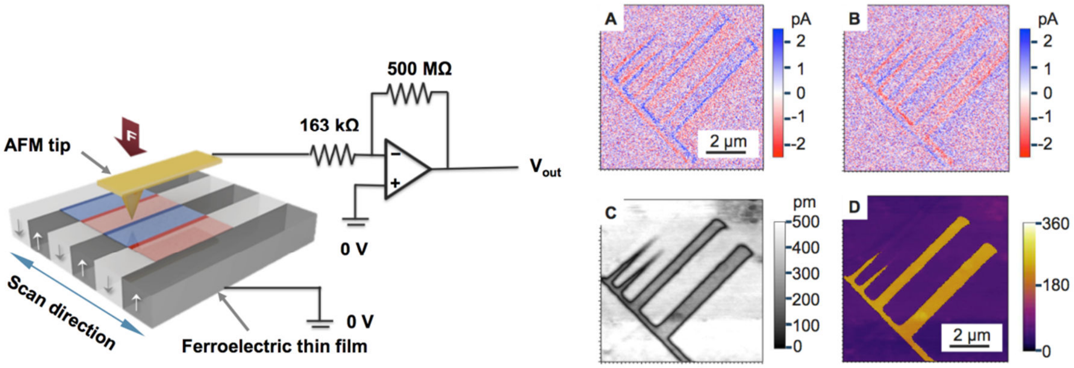

Fig. 1: (left) *Schematic diagram of CGM and (right) trace and retrace CGM images of artificially decorated domains with different sizes. CGM images taken on ribbon shaped domains poled by 6 V to the bottom electrode of 85 nm thick $LiTaO_3$ films (A) from left to right scan (trace) and (B) from right to left scan (retrace) using Pt tips at scan frequency of 40 Hz. PFM (C) amplitude and (D) phase images are taken at the same region at scan frequency of 1 Hz where bright phase contrast corresponds to positive (upward) domain and dark phase contrast to negative (downward) domain.*

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[1] E-mails: hong@anl.gov & aroelofs@anl.gov

Enhancement of Local Piezoresponse in Polymer Ferroelectrics via Nanoscale Control of Microstructure

Yoon-Young Choi[1], Pankaj Sharma[2], Charudatta Phatak[1], David J. Gosztola[3], Yunya Liu[4], Joonseok Lee[3], Jiangyu Li[5], Alexei Gruverman[2], Stephen Ducharme[2] and Seungbum Hong[1*]

[1]Materials Science Division, Argonne National Laboratory, 60439, Lemont, IL, USA
[2]Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience, University of Nebraska, 68588-0299, Lincoln, NE, USA
[3]Center for Nanoscale Materials, Argonne National Laboratory, 60439, Lemont, IL, USA
[4]Faculty of Materials, Optoelectronics and Physics, Xiangtan University, Hunan 411105, P. R. China
[5]Department of Mechanical Engineering, University of Washington, 98195, Seattle, WA, USA

As flexible smart devices are being developed and distributed, most of the rigid components such as ceramic piezoelectric materials used for actuating components are expected to be replaced by flexible materials such as polymer ferroelectric materials. However, one of the biggest challenges for polymer ferroelectric materials is their low piezoelectric coefficient. Here we present a mechanical annealing process using a nanoscale tip, which can increase the local piezoelectric properties by 86% higher than the thermally crystallized film without mechanical annealing. This process can control the material properties over large area in the films with thickness down to 50 nm through sequential spatial integration of local interactions between the nanoscale tip and the films at room-temperature.

Our mechanical annealing process uses high mechanical stress ranging from 212 MPa to 495 MPa which can induce irreversible plastic deformation to 50-nm thick P(VDF-TrFE) thin film. However, the surface morphology did not show any sign of significant damage or delamination, and changed from randomly oriented to well-aligned lamellar crystals. Furthermore, the piezoelectric properties were enhanced in terms of out-of-plane (OP) and in-plane (IP) remanent pieozoresponses (OP piezoresponse: 28 ± 7 pm/V and IP piezoresponse: 101 ± 33 (a.u.)) when compared with those of annealed P(VDF-TrFE) thin films (OP piezoresponse: 15 ± 4 pm/V and IP piezoresponse: 44 ± 21 (a.u.)).

In order to understand the mechanism behind the mechanical annealing process, we conducted Raman spectroscopy and piezoresponse force microscopy (PFM) imaging experiments. We found that the amount of β-phase with long trans sequences increases and α-phase with trans-gauche conformation appears. In addition, the polarization aligns toward the in-plane direction perpendicular to scan axis during mechanical annealing, indicative of polarization change induced by mechanical stimulus. We believe, therefore, that this new technique is very important not only from the perspective that we can locally control the piezoelectric properties and induce molecular alignments but also from the point of view that we can fabricate high performance piezoelectric devices.

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works,distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. The work of Raman spectroscopy, SEM and TEM imaging was performed at the Center for Nanoscale Materials and Electron Microscopy Center, a US Department of Energy, Office of Science, Office of Basic Energy Sciences User Facilities under Contract DE-AC02-06CH11357. The work at the University of Nebraska (P.S., A.G., S.D.) was supported by the Department of Energy U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0004530, by the National Science Foundation through the Materials Research Science and Engineering Center (Grant No. DMR-0820521).

Introducing nano-FTIR – Infrared Imaging and Spectroscopy at 10nm Spatial Resolution

T.Gokus[1], F. Huth[1], M. Diem[1], S. Schiefer[1] and A.J.Huber[1]

[1]*Neaspec GmbH, Bunsenstrasse 5, 82152 Planegg (Munich), Germany*

Neaspec's near-field optical microscopy systems (NeaSNOM) allow to overcome the diffraction limit of classical optical microscopy and spectroscopy enabling optical measurements at a spatial resolution of 10nm not only at visible frequencies but also in the infrared or terahertz spectral range.

Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) [1] employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample material and detection of the elastically tip-scattered light yields nanoscale resolved near-field images simultaneous to topography.

Development of a dedicated Fourier-transform detection module for analyzing light scattered from the tip which is illuminated by a broadband laser source enabled IR spectroscopy of complex nanostructures (nano-FTIR) [2]. Identification of polymers [2], analysis of embedded structural phases in biominerals [3], or investigation of the secondary structure of individual protein complexes [4] demonstrated the successful application of nano-FTIR as a material characterization technology. Equipping NeaSNOM systems with cw-light sources near-field imaging can be performed at time scales of 30-300s per image. Patented signal detection and analysis technology allows i.e. investigation of phase change materials, analysis of Graphene nanostructures [5], or to study energy storage materials in near-field amplitude and phase at unprecedented scanning speed and signal quality.

The patented modular system design enables tailored system configurations where the ultimate spectral coverage can be achieved by using synchrotron-based broadband IR light sources [6]. Based on reflective optics design of the system novel time-resolved near-field measurements [7] or the integration of THz-TDS systems have been realized.

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[Invited] Scanning Tunneling Microscopy of Iron on Manganese Nitride and on Gallium Nitride Surfaces

Andrada-Oana Mandru[1], Wenzhi Lin[1], Arthur R. Smith[1], Hamad A. H. Al-Brithen[1], Jonathan G. Sanchez[2,3], and Noboru Takeuchi[3]

[1]Nanoscale & Quantum Phenomena Institute, Department of Physics & Astronomy, Ohio University, Athens, OH 45701
[2]Benemèrita Universidad Autònoma de Puebla, Instituto de Física "Ing Luis Rivera Terrazas", Apartado Postal J-48, Puebla 72570, Mèxico
[3]Centro de Nanociencias y Nanotecnologia, Universidad Nacional Autònoma de Mèxico, Apartado Postal 14, Ensenada Baja California, Codigo Postal 22800, Mèxico

Ferromagnetic layers on either antiferromagnetic or semiconducting layers are each systems of great interest technologically. In this work, we apply both spin-polarized and normal scanning tunneling microscopy to investigate the initial stages of Fe deposition on (a) a semiconductor surface [GaN(0001)] and (b) an aFM nitride surface [Mn_3N_2(001)]. Probe tips consist of either W tips or W tips coated with Fe. In all cases, the freshly prepared sample is transferred through ultra-high vacuum directly into the adjoining SP-STM system. In the case of Fe on GaN pseudo-1×1 (1 + 1/12), STM imaging shows 6×6 regions adhering to single and double height GaN steps. A combination of STM and first-principles theory suggest that deposited Fe incorporates within the top (or 1st) Ga layer, displacing Ga atoms which, after cooling from the deposition temperature, lead to a relaxed and highly distorted Ga dimer structure. In the case of Fe on Mn_3N_2(001), STM imaging shows single monolayer height islands on the surface; however, Auger electron spectroscopy finds a very tiny Fe:Mn ratio, in agreement with theoretical calculations showing that Fe is unstable on this surface and diffuses into sub-surface Mn layers. Funding is provided by DOE-BES (No. DE-FG02-06ER46317) (Fe/semiconductors) and NSF-DMR (No. 1206636) (Fe/antiferromagnets).

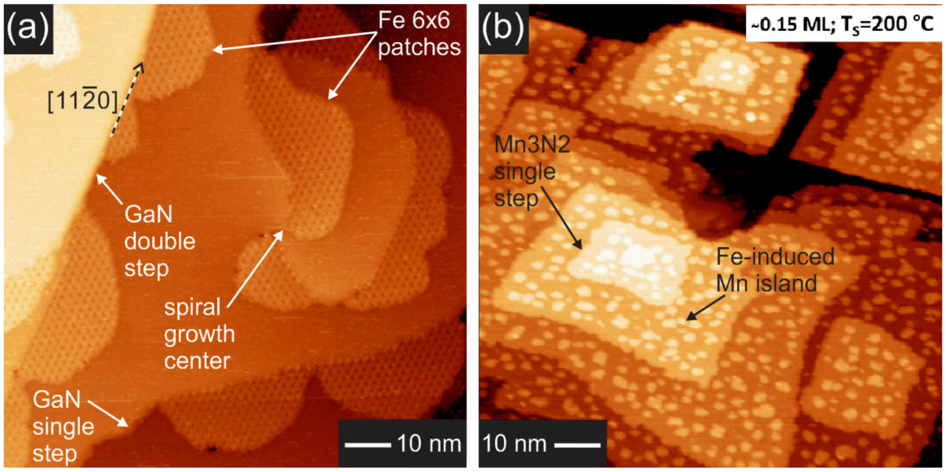

Fig. 1: *STM images of Fe on (a) GaN pseudo-1x1 1+1/12 surface; and (b) Mn_3N_2 (001) surface.*

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Tuning Magnetic Anisotropy and Kondo Screening in a Hund's Impurity by Controlled Hydrogenation

A. A. Khajetoorians[1], M. Steinbrecher[1], M. Valentyuk[2], T. Schlenk[1], A. Lichtenstein[2], T. O. Wehling[3], J. Wiebe[1] and R. Wiesendanger[1]

[†] Institute of Applied Physics, Hamburg University, D-20355 Hamburg, Germany

[‡] I. Institute of Theoretical Physics, Hamburg University, D-20355 Hamburg, Germany

[*] Bremen Center for Computational Materials Science and Institute for Theoretical Physics, University of Bremen, D-28359 Bremen, Germany

A possible building block of a future nanospintronic device is an individual atom adsorbed onto the surface of a metal (adatom) [1]. Its magnetic properties can be tailored by a proper combination of adatom and substrate species, which governs the interplay between intra-atomic (Hund's rule) exchange, spin-orbit coupling and crystal field induced magnetic anisotropy and Kondo-coupling to the substrate conduction electron bath. The magnetic anisotropy leads to a stabilization of the local adatomic spin into particular directions. On the other hand, this spin is destabilized by the Kondo coupling which might ultimately lead to a complete quenching of the magnetic moment for strong hybridization between adatom and substrate states.

Here, we show using inelastic scanning tunneling spectroscopy in comparison to *ab-initio* calculations, that Fe adatoms on Pt(111) [2], which are in the strong hybridization limit, maintain a well-defined magnetic moment stabilized by Hund's rule exchange. However, fluctuations in the orbital occupation of this so called Hund's impurity [3] provoke that the local spin is not a good quantum number anymore. Moreover, controlled hydrogenation of the Fe adatom can tune its magnetism into a critical state, where magnetic anisotropy is competing with Kondo screening. The measured temperature and magnetic field dependencies of the spectral functions of this interesting impurity show deviations from existing spin-1/2 Kondo theories and are thus an ideal test for the development of multi-orbital Kondo theories, which are still in their infancies.

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Reversible Control of Single Molecule Kondo Interactions

Yang Li[1, 2], Andrew DiLullo[1], Brandon Fisher[1], Saw-Wai Hla[1, 2]

[1]*Argonne National Lab, 60439, Lemont, USA*
[2]*Ohio University, 45701, Athens, USA*

A porphyrin derivative, Co-TBrPP, is known to exhibit Kondo resonance originated from the many-body spin-electron interactions on some metallic surfaces [1,2]. We demonstrate here a reversible controlled extinctions and formations of a spectroscopically observed Kondo interaction for single TBrPP-Co molecules adsorbed on a Au(111) substrate. The Kondo state switching is achieved by positioning the TBrPP-Co molecules at various positions on the herringbone reconstruction of the Au(111) surface by lateral positioning of the molecules using a scanning tunneling microscope (STM) tip. The spectroscopic manifestation of the Kondo interaction, which appears for molecules on HCP and FCC regions of the Au(111) surface, is not present for molecules manipulated onto the herringbone elbow locations (Fig. 1). It is well known that Kondo interactions are geometry dependent [3]; we examine possible causes for the resultant site specific spin interaction.

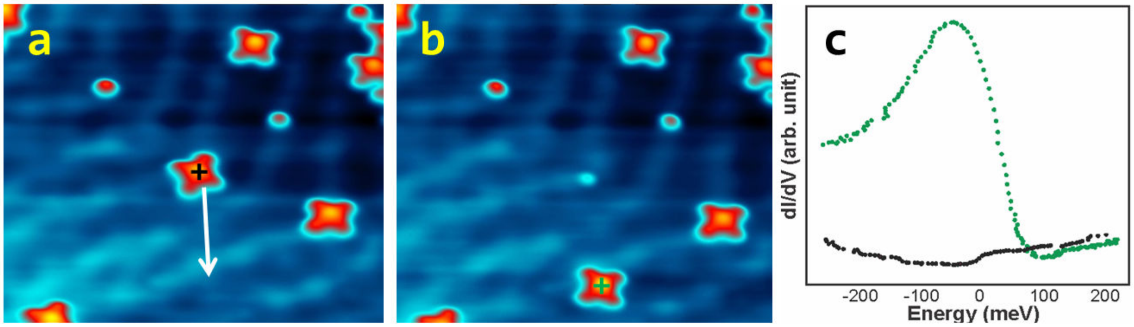

Fig. 1: *(a) STM image of a TBrPP-Co molecule located at a herringbone elbow position. (b) The molecule is laterally moved to a close packed region of a Au(111). (c) Differential tunneling conductance data taken at the molecule's cobalt ion sites in (a) and (b) are presented as black and green spectra, respectively.*

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[Invited] Probing Ultrafast Spin Dynamics by Optical Pump-Probe STM

Hidemi Shigekawa

Faculty of Pure and Applied Science, University of Tsukuba, Japan

The studies of spin dynamics in low-dimensional systems have grown into a rapidly developing and important area from fundamental and practical points of view. In this talk, we demonstrate the optical pump-probe STM (OPP-STM) technique, which enables the nanoscale probing of spin dynamics with the temporal resolution corresponding to the optical pulse width in principle.

In nanoscale science and technology, the addition of high temporal resolution to scanning probe microscopy (SPM) has been attracting considerable attention since its invention We have been developing a microscopy technique that simultaneously realizes the spatial resolution of scanning tunneling microscopy (STM) and the temporal resolution of ultrashort-pulse laser technology, optical pump-probe (OPP) method [1-7]. The combination of STM with optical technology has advantages to enable the analysis of photo-induced dynamics on the nanoscale as well as the realization of ultrafast time-resolved microscopy. In OPP-STM, a non-equilibrium carrier distribution is generated using ultrashort laser pulses and its relaxation processes are probed by STM using the OPP method realized in STM. By combining the microscopy with atom tracking technique, even a single-atomic-level analysis of the carrier dynamics has become possible [5-7].

With the development of a new modulation technique of circularly polarized light, detection of spin dynamics has been realized [8]. The relaxation of spins optically oriented in single quantum wells formed by GaAs/AlGaAs was observed independently. Furthermore, spin precession in GaA under magnetic field was successfully probed using tunneling current by the time-resolved STM. Details will be discussed with the recent results at the conference.

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http:dora.bk.tsukuba.ac.jp, hidemi@ims.tsukuba.ac.jp

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Optical Processes in Isolated Phthalocyanines Probed by Scanning Tunneling Luminescence Spectroscopy

H.Imada[1], M. Imai[1, 2], T. K. Shimizu[3], M. Kawai[2], Y. Kim[1]

[1]Surface and Interface Science Laboratory, RIKEN,
351-0198, 2-1 Hirosawa, Wako, Saitama, Japan
[2]Department of Advanced Materials Science, The University of Tokyo,
277-8561, 5-1-5 Kashiwanoha, Kashiwa, Chiba, Japan
[3]National Institute for Materials Science,
305-0047, 1-2-1 Sengen, Tsukuba, Ibaraki, Japan

We are working on atomic-scale investigation of energetics (energy conversion and transport) in molecular systems using scanning tunneling microscopy (STM) combined with a photon detection system. The combination of STM with luminescence spectroscopy provides us a powerful tool to unveil fundamental processes occurring at nano-scale [1-3]. Our aim in this work is to examine optical processes in a single molecule which is electrically isolated from a metal substrate.

Metal-free phthalocyanine (H_2Pc) was deposited on ultrathin NaCl films grown on a Ag(111) surface (Fig.1). It is suggested from scanning tunneling spectroscopy (STS) measurement that the molecule is electrically isolated from the Ag(111) substrate when the molecule is adsorbed on ultrathin NaCl films. Luminescence spectra were measured by injecting electrons from an STM tip to single H_2Pcs. When a H_2Pc is directly adsorbed on the Ag(111) substrate, the luminescence spectrum is dominated by tip-induced plasmon emission having a single broad luminescence peak. However, H_2Pc starts to exhibit sharp intrinsic fluorescence when it is adsorbed on a NaCl thin film. The luminescence spectrum consists of a main peak and small sub peaks on the lower energy side. The emission peaks were attributed to the molecular fluorescence by electronic transition from the first excited singlet state to the vibrationally excited and ground states of the electronically ground state.

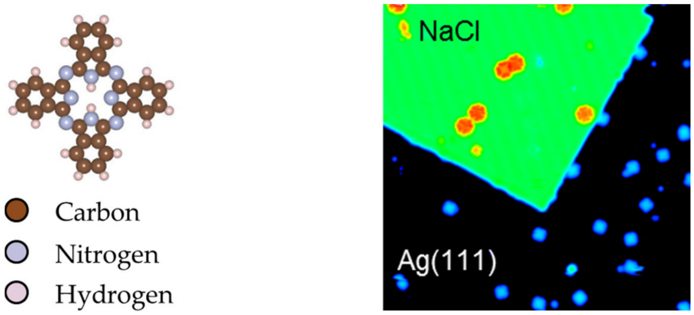

Fig. 1: *Molecular structure and an STM image of H_2Pc. The STM image shows H_2Pcs adsorbed on a NaCl film as well as on the Ag(111) substrate (Tunneling current = 3 pA, Sample bias voltage = 2 V, Scan area = 40×40 nm^2).*

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Cathodoluminescence of Plasmonic Crystals and Cavities

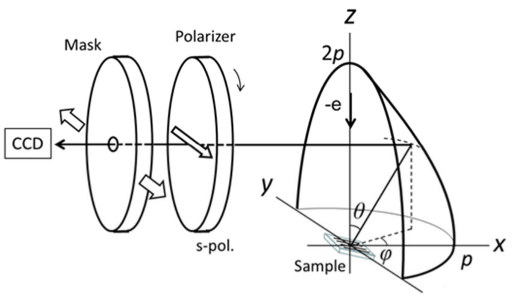
N. Yamamoto[1,2] and H. Saito[1]

[1]*Tokyo Institute of Technology, 152-8551, Tokyo, Japan*
[2]*JST-CREST, 332-0012, Saitama , Japan*

High resolution cathodoluminescence (CL) technique combined with a scanning transmission electron microscope (STEM) is useful for investigating physical property of surface plasmons in nano-structures by detecting an emitted light due to interaction between high energy electrons and plasmons. Light emission induced by surface plasmons in metal surface structures has been studied by the STEM-CL technique with a high spatial resolution of nanometer scale [1]. Resolution of STEM-CL is mainly limited by a probe size of the electron beam, and is typically in the order of 1 nm.

Surface plasmon polariton (SPP) is a longitudinal surface charge wave propagating through a dielectric-metal interface, which can be excited by high energy electrons and is converted to photons when propagating on the interface structures. Light emitted from a specimen in the STEM is collected by a parabolic mirror, and is detected by a CCD detector (Fig.1). Plasmonic crystals with periodic structures and cavities were fabricated on semiconductor substrates by electron beam lithography and silver was thermally deposited on them. 1D and 2D plasmonic crystals were made with various terrace width (*D*) to period (*P*) ratios, and dependence of their band gap on the D/P ratio was measured from the angle-resolved spectral (ARS) patterns and photon maps (Fig.2) [2]. Properties of plasmonic cavities in the 1D and 2D plasmonic crystals were investigated. Light emission property of SPPs is sensitive to material overlaid on the nano-structures, which was also studied by the CL technique.

This work was supported by MEXT Nanotechnology platform.



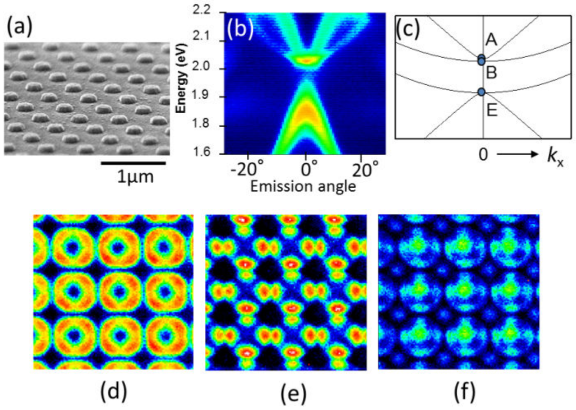


Fig. 1: Arrangement of the ARS measurement

Fig. 2: (a) 2D plasmonic crystal with a squared lattice (period of 600 nm), (b) ARS pattern, (c) dispersion relation near the Γpoint, (d)-(f) photon maps at the resonant energies.

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31 July 2014 Thursday (Morning Sessions)

[Invited] Scanning Tunneling Spectroscopy of Single Crystal Superconductors and Molecular Adsorbates

Katharina J. Franke
Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Scanning tunneling microscopy (STM) gained uttermost importance for the resolution of atomic-scale structures on surfaces and for the unveiling of their electronic density of states in real space. One drawback of this technique is that information about the k-dependence of the electronic band structure is hardly accessible, despite from imaging and Fourier transforming patterns of electron scattering. Recently, it has been shown that the focusing of electron waves from subsurface impurities can be used to map the Fermi surface in real space of a one-band conductor [1]. However, many materials possess more complex Fermi surfaces, which may be influenced individually by adsorbates or defects on the surface. Here, we use scanning tunneling microscopy and spectroscopy at 1.2 K to experimentally probe the Fermi surface of lead (Pb) single crystals. Pb is a strong-coupling s-wave BCS superconductor with two separated Fermi sheets of different character, namely s-p- and p-dlike [2]. In the tunneling spectrum, we observe for all surfaces two quasi-particle resonances at each side of the superconducting energy gap, which are due to the two different superconducting gap parameters. They have an energy difference of 150 μV and differ remarkably in intensity. We use dI/dV mapping around subsurface defects to characterize the two Fermi surfaces in real space. Lead adatoms substantially influence the intensity of the excitation peaks. This reflects the different localization character of the two Fermi surface sheets. The superconducting gap properties can further be utilized to increase spin excitation lifetimes of magnetic adsorbates on the surface, where the gap prohibits efficient pathways of energy quenching into the substrate [3].

In the last part of the talk, we will employ scanning tunneling microscopy to resolve the interplay of the local surrounding on the magnetic properties of individual atoms. Fe-Octaethylporphyrin (FeOEP) is a metal-organic macrocycle, whose magnetic properties can be probed by a characteristic fingerprint close to the Fermi level in tunneling spectroscopy. A temperatureinduced step-wise electrocyclic ring closure of the ethyl groups results in the final product Fe-Tetrabenzoporphyrin (FeTBP). The chemical modification is accompanied by an increased magnetic interaction with the metallic substrate as resolved by changes in the shape and width of a Kondo resonance [4].

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Real-space Observations of Superconducting Proximity Effect by Scanning Tunneling Microscopy and Spectroscopy

Howon Kim[1], Shi-Zeng Lin[2], Matthias J. Graf[2], Takeo Kato[1], and Yukio Hasegawa[1]

[1]*The Institute for Solid State Physics, The University of Tokyo, 5-1-5, Kashiwa-no-ha, Kashiwa, 277-8581 Japan*

[2]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

In this study, we investigated superconducting proximity effect at the interface between superconducting two-dimensional (2D) Pb islands and a single-atomic-layer surface metal, known as the striped incommensurate (SIC) phase of Pb formed on Si(111) surfaces by performing local tunneling spectroscopy with a low temperature scanning tunneling microscope (STM). We observed tunneling spectra with an induced gap-like shape in the normal metal side around superconducting islands and spatial decaying behaviors of the induced gap with the distance from the superconductor-normal metal boundary. Additionally, we studied influences of the presence of local surface structures on the normal metal, which is expected to modify the proximity effect. The experimental results are compared with the predictions of the quasi-classical theory based on the Usadel equation. [1]

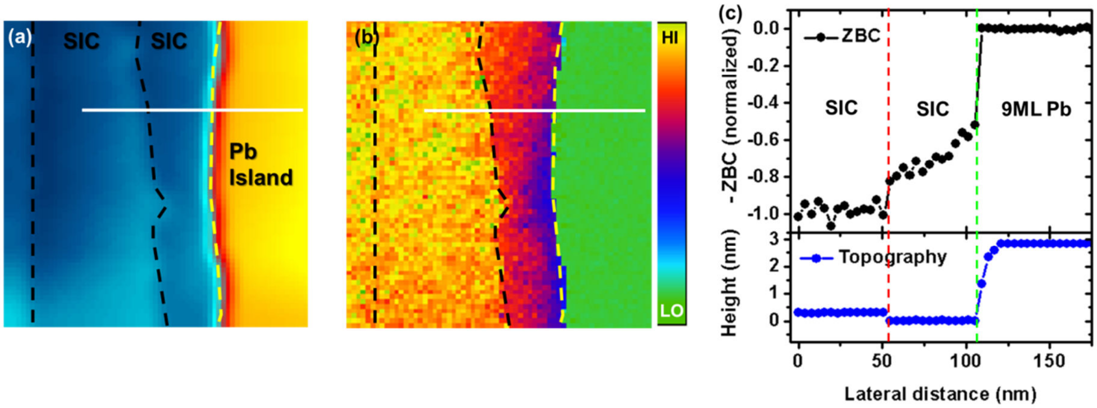

Fig. 1: *(a) a STM topography image of a 9ML-thick Pb island sitting on the stepped Pb-SIC film on Si(111). (b) a zero-bias conductance (ZBC) map for the same area of (a). (c) Surface profiles along the lines (white) in (a) and (b). Red and green dotted lines are guide lines for the step boundary on the SIC surface and interface between SIC film and a Pb island, respectively. (upper) normalized ZBC and (lower) topography*

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A Superconducting Raft in the Fermi Sea

Kyaw Zin Latt[1], Sajida Khan[1], Hao Chang[1], Abdou Hassanien[2], and Saw-Wai Hla[1,3]

[1] *Nanoscale and Quantum Phenomena Institute, Physics & Astronomy Department, Ohio University, Athens, OH 45701, USA.*

[2] *National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia.*

[3] *Center for Nanoscale Materials, Argonne National Laboratory, 9700 S Cass Ave, Lemont, IL 60439, USA.*

We report a new organization of nanoscale molecular clusters that exhibit superconducting properties on Ag(111) substrate below 8K temperature. These small two dimensional crystallites are composed of a few molecular chains formed by polymerized BETS (donors) and $GaCl_4$ (acceptor). In STM images, these molecular clusters appear as ordered parallel chains resembling the 'rafts'. Using scanning tunneling microscope (STM) manipulation, small molecular clusters having a few donor-acceptor chains are laterally manipulated to bare surface area. From the tip height signals, the dynamics of molecular clusters during their movements across the surface has been unveiled. Repeated manipulation experiments reveal that the rafts move only along [211] surface directions with single atomic site hops. Then by means of tunneling spectroscopy, interaction of two dimensional surface state electrons with these two dimensional clusters are investigated at the molecule-metal boundary regions. The results provide how electrons interact with the superconducting clusters in addition to the electronic and mechanical properties of these superconducting rafts. This work is financially supported by the US DOE, BES grant number: DE-FG02-02ER46012.

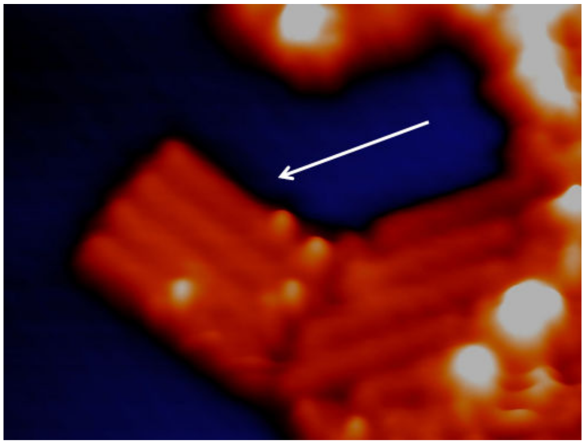

Fig. 1: *STM image showing an extracted molecular raft composed of four molecular chains on Ag(111).*

[Invited] Prospects for Hydrogen Storage in Graphene

S. Heun

NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, 56127 Pisa, Italy

The realization of innovative hydrogen storage materials has worldwide strategic importance. Graphene has recently attracted attention as a promising hydrogen storage medium. Indeed, graphene is lightweight, chemically stable, and exhibits attractive physico-chemical properties for hydrogen adsorption. Furthermore, the interaction between hydrogen and graphene can be controlled by chemical functionalization.

The energetics of the chemisorption of hydrogen on graphene can be modified by the local curvature of the graphene sheet. Based on scanning tunneling microscopy (STM) we report on site-selective adsorption of atomic hydrogen on convexly warped regions of monolayer graphene grown on SiC(0001). This system exhibits an intrinsic curvature owing to the interaction with the substrate [1]. We show that at low coverage hydrogen is found on convex areas of the graphene lattice [2]. No hydrogen is detected on concave regions. These findings are in agreement with theoretical models which suggest that both binding energy and adsorption barrier can be tuned by controlling the local curvature of the graphene lattice. This curvature-dependence combined with the known graphene flexibility may be exploited for storage and controlled release of hydrogen at room temperature.

Theoretical studies regarding metal atoms (e.g. Ti) deposited on graphene suggest that such materials can adsorb up to 8 wt% gravimetric density of hydrogen. We investigate the deposition of Ti on graphene and its potential for hydrogen storage [3]. The Ti atoms form small islands (diameter ~ 10 nm). The Ti-covered graphene was exposed to molecular hydrogen, and then the sample temperature was increased while measuring the mass-sensitive desorption. The desorption spectra show two peaks at 210ºC and 290ºC. Their intensity increases with increasing Ti coverage. Our data demonstrate the stability of hydrogen binding at room temperature and show that the hydrogen desorbes at moderate temperatures – both ideally matching technical requirements for hydrogen storage. To further increase the hydrogen uptake of these samples we are now working on increasing the active surface for hydrogen adsorption by decreasing the size of the Ti-islands and increasing their density.

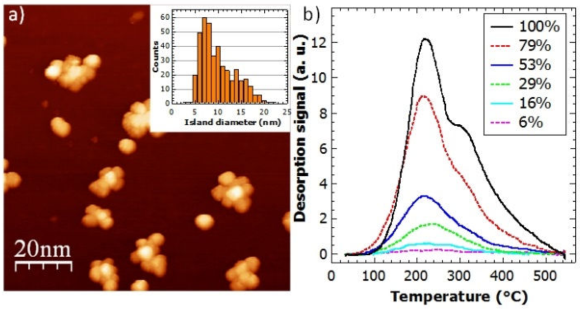

Fig. 1: *a) 100 x 100 nm^2 UHV-STM image of a graphene surface with a titanium coverage of 16% (V = 2 V, I = 280 pA). The titanium atoms form small islands with a size distribution as shown in the inset. b) Desorption spectra measured for different coverages of titanium. The amount of stored hydrogen increases with Ti-coverage.*

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First Principles Analysis of Defect-Mediated Li Adsorption on Graphene

Handan Yildirim[1], Zhijian Zhao[1], Alper Kinaci[2], Maria K.Y. Chan[2], Jeffrey P. Greeley[1]

[1]Purdue University, School of Chemical Engineering Department, West Lafayette IN, USA
[2]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA

Since the discovery of freestanding graphene, this 2D structure is considered as a potential alternative for graphite, because of its outstanding electronic and mechanical properties. It has attracted much attention as a promising electrode material for electrochemical energy storage devices such as Li-ion batteries due to high surface area and superior electronic conductivity. For Li-ion battery applications, graphene is used as a buffer layer to suppress the large volume expansion observed in high capacity anode materials and as a coating material to enhance conductivity. It was shown that graphene sheets prepared by reduction of graphite oxide (GO) deliver a reversible capacity and good cycling stability. Large variation in the capacity is reported by several studies for graphene, which is prepared with the exact similar techniques. Such discrepancy is suggested to result from the disordered and/or ordered structure of graphene sheets affecting Li storage capacity, and hence suggesting that the structural characteristics influence the resulting electrochemical performance.

Earlier experimental studies have identified the existence of defects such as Stone-Wales and double vacancy defects, as well as grain boundaries in graphene. Thus, for complete understanding of the electrochemical performance of graphene, the role of different types of defects on the electrochemical performance should be identified as well as the defect density influence should be evaluated. Such comparative study along with pristine graphene can provide vast amount of information not only for the electrochemical performance, but also, for the structural and electronic structure differences with the types of defects, defect densities, and Li concentration.

In this talk, we will present density functional theory results on the atomistic level understanding of the interaction between Li and the graphene with topological defects, and their role on the electrochemical performance. Li configurations are generated combining an algorithm whose results are tested using a genetic algorithm method. We explore the effect of each defect type on the adsorption of Li on graphene. The electrochemical performance of these defective sheets under varying Li concentration is studied, and compared with those obtained for the pristine graphene. Furthermore, the effect of defect density on the electrochemical performance is evaluated. Lithiation voltages and capacities as function of each defect type will be reported, and compared with those of the pristine graphene. The results are expected to shed light on the role of each defect type on the electrochemical performance of graphene as an alternative anode material for Li ion batteries.

Molecular Sensing at Graphene Grain Boundaries

Poya Yasaei[1], Bijandra Kumar[1], Artem Baskin[2], Nikita Repnin[2], Petr Král[2], Amin Salehi-Khojin[1,*]
[1] *Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, IL, 60607, USA.*
[2] *Department of Chemistry, University of Illinois at Chicago, Chicago, IL, 60607, USA.*
[*] Corresponding author, salehikh@uic.edu,

In principle, topological defects improve the sensitivity of carbon-based chemical sensors toward gas molecules due to an efficient physisorption and enhanced charge transfer process. Since such defects are formed within a single crystalline graphene lattice, they have a modest effect on electronic properties of the device. Grain boundaries (GBs) in graphene are different from other defect types as they form between misoriented crystalline grains, which can potentially give rise to electronic transport gaps. The emergence of transmission gaps in graphene GBs can be employed to acquire an on/off like behavior for the passage of charge carriers upon exposure to gas molecules. In this work, for the first time, we have isolated an individual GB in order to study the role of this transport gap on the chemical response of GBs, and observed an ultra-high sensitivity of individual GBs to adsorbed dimethyl methylphosphonate (DMMP) or 1,2-dichlorobenzene (DCB) molecules. It has been shown that an isolated graphene GB has ~300 times higher sensitivity to analyte molecules than defective single crystalline grains. We also investigated the sensing response of a sequence of multiple GBs, naturally formed by the merging of the grains in the CVD growth, and observed a sensitivity crossover from a single GB to a large-area polycrystalline graphene. This study clearly demonstrates an inherent limitation of the polycrystalline graphene sensors compared to an individual GB sensor with a high degree of isolation. Our hybrid modeling of an electronic structure and transport in realistic GBs reveals that the ultra-sensitivity in GBs is caused by a synergetic combination of gas molecules accumulation at GB, together with the existence of ultrasensitive switchable transport channels in GBs. The discovered sensing platform opens up new pathways for the design of nanometer scale highly sensitive chemical detectors.