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NUS National University of Singapore

A*STAR Institute of Materials Research and Engineering

IAMNano 2017

IAMNano 2017

International Workshop on Advanced and In-situ Microscopies of Functional Nanomaterials and Devices

NUS University Hall Auditorium
12-15 Nov. 2017, Singapore

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Cover image:
Coloured HAADF image of La atoms (bright) located at a TiO_2 grain boundary. The viewed area is 3.0 × 4.3 nm (W × H). Courtesy of Dr Chunhua Tang, National University of Singapore

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Dear Colleagues,

On behalf of the International Advisory Board and the Local Organizing Committee it is my great pleasure to welcome you to the 3rd International Workshop on Advanced and In-situ Microscopies of Functional Nanomaterials and Devices, (IAMNano 2017), to be held this year in Singapore.

Following the tradition of the first two IAMNano meetings, the meeting will consist of 43 excellent invited oral presentations, plus numerous excellent contributed poster presentations. We have also included some technical presentations from a number of microscopy companies, and we hope that you will find the whole scientific program illuminating and inspiring for future research directions. We also hope that you will not only take the opportunity for networking with colleagues and friends but also take some time before or after the program to enjoy Singapore, Asia's most popular conference destination. Furthermore we hope that you take advantage of the Tuesday evening tour and conference dinner where you can taste some of the history and flavour of Singapore.

I wish you a productive meeting, and welcome to IAMNano 2017!

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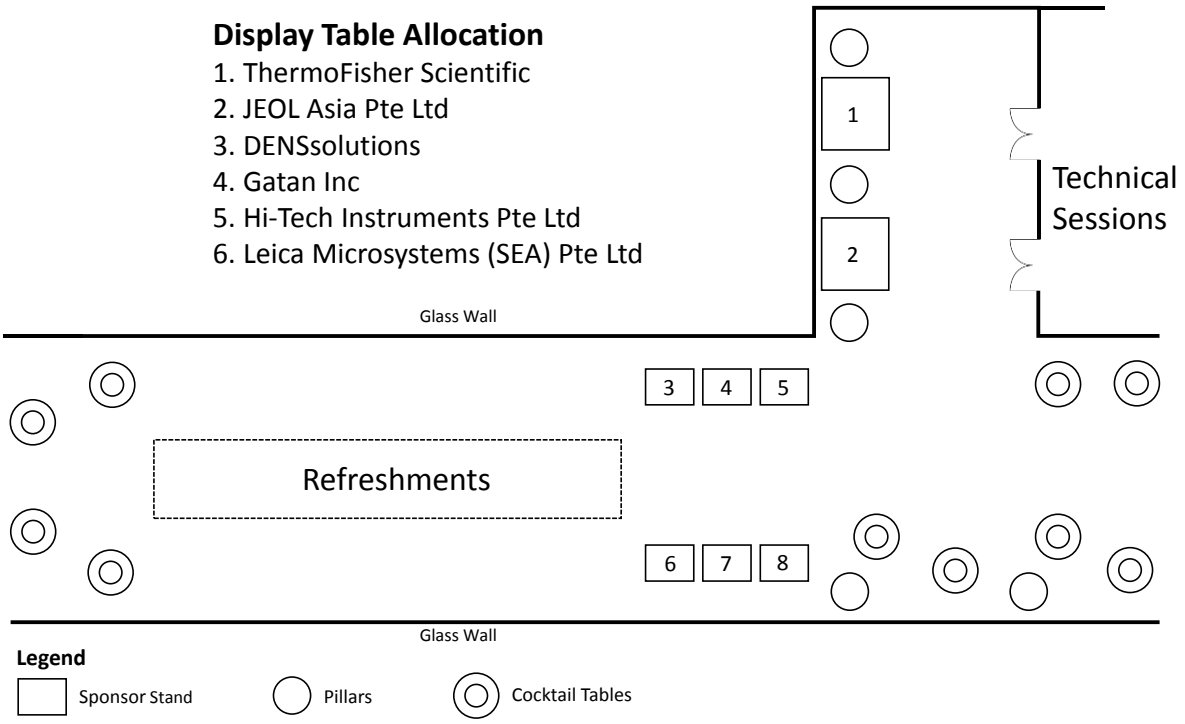

Hotel (and IAMNano **venue for Sunday**):

Hotel Park Avenue Rochester
31 Rochester Drive,
Singapore 138637
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Nearest MRT (underground train station): Buona Vista

IAMNano **venue for Monday-Wednesday**:

University Hall Auditorium,
National University of Singapore
Lee Kong Chian Wing Level 2,
21 Lower Kent Ridge Rd,
Singapore 119077

For maps: see next page

A free shuttle bus connects the NUS University Hall with the Hotel following this schedule:

Day	Hotel to NUS	NUS to Hotel
Sunday 12 Nov	No bus: the IAMNano sessions will be held on Sunday at the Hotel Park Avenue Rochester	
Monday, 13 Nov	Departs 08:00	Departs 19:00
Tuesday, 14 Nov	Departs 08:00	Departs 17:45 from NUS to Conference Dinner*
Wednesday, 15 Nov	Departs 08:00	Departs 12:40

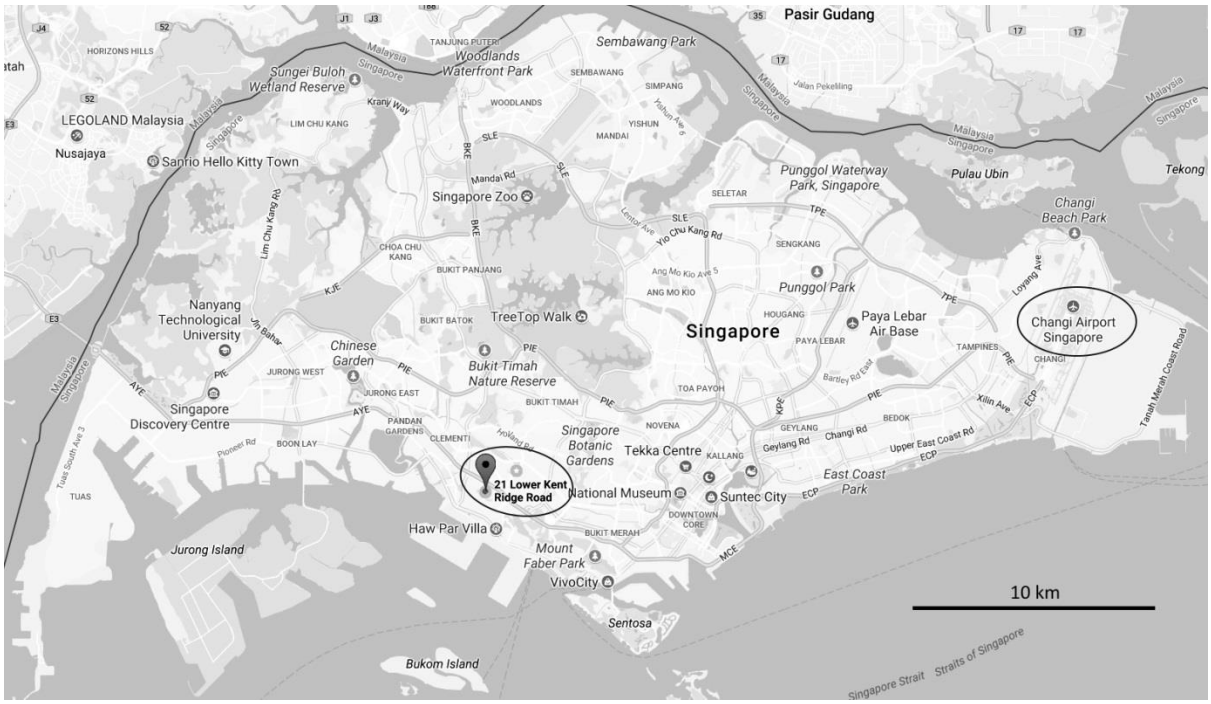
*Itinerary for the Conference Dinner:
17:45 Depart NUS University Hall to Merlion Park for River Cruise
19:00 Dinner at Grand Shanghai restaurant
21:00 Depart Grand Shanghai restaurant to Park Avenue Hotel

A taxi drive between the hotel and the NUS University Hall will take ~5 minutes and should cost around S$ 6-9.

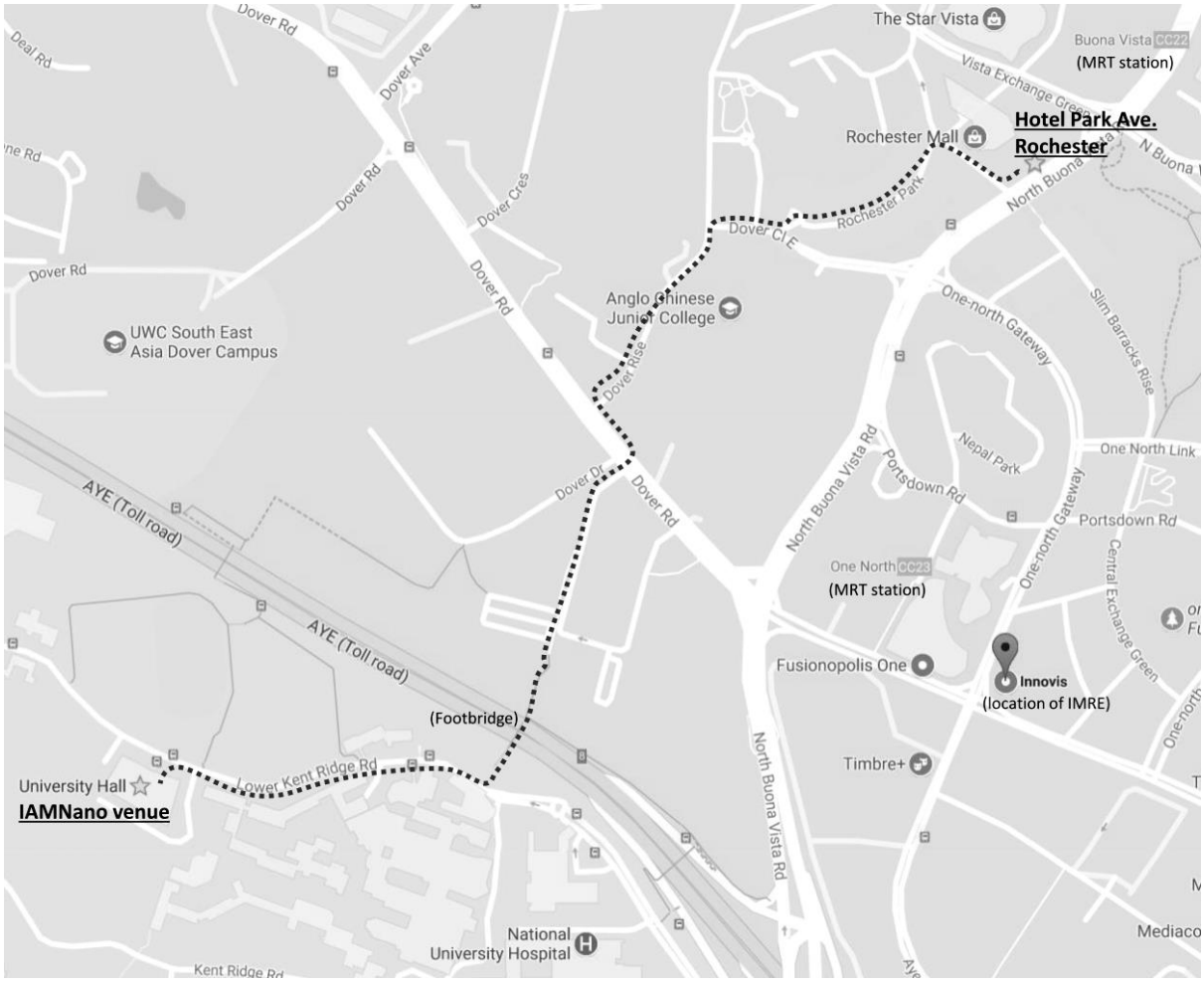
The Downtown Area (Chinatown, Little India, Marina Bay, Clarke Quay) is a ~15 minutes taxi drive away, costing around S$ 20.
Changi Airport is in the north-east of the country and will take ~30 minutes by taxi, costing around S$ 30.

Ride-hailing services are also available in Singapore: (1) Grab taxi, and (2) Uber

Public transport is efficient and inexpensive. Buses and MRT trains use the same ticketing system, the "EZ-Link card", which can be purchased at MRT stations.



The NUS University Hall is located on the Kent Ridge campus of NUS, the National University of Singapore, which is located in the south-west of the country, circled in the map above. Below: a ~25 minutes walking route between the hotel and the NUS University Hall.



SUNDAY, November 12		**Location: Hotel Park Avenue Rochester**
15:00-15:30	Registration, Opening Ceremony and Remarks	
16:00-16:25	Robert Sinclair	In situ high resolution and environmental electron microscopy studies of material reactions
16:25-16:50	Max Haider	Instrumental developments for high-resolution in-situ Electron Microscopy: opportunities and limitations
16:50-17:15	Tracy Lovejoy	Ultra-high spatial and energy resolution STEM/EELS
17:15-17:40	Joachim Mayer	Nanoswitches: TEM characterization of resistively switching oxides
17:40-18:05	Yu Han	High-resolution transmission electron microscopy of electron beam-sensitive crystalline materials
18:05-19:30	Welcome Reception	

MONDAY, November 13		**Location: NUS University Hall Auditorium**
8:00-8:30	Registration	
8:30-8:55	Gianluigi Botton	Probing the electronic structure of solids with EELS
8:55-9:20	Ferdinand Hofer	Direct imaging of channel constituents in beryl
9:20-9:45	David Smith	Studying Heteroepitaxial Compound Semiconductors
9:45-10:10	Nestor Zaluzec	XEDS Applied to Soft-Hard/Matter Measurements at the Nanoscale in the Next Generation AEM
10:10-10:40	Coffee Break	
10:40-11:05	Kazu Suenaga	Low-voltage STEM-EELS characterization of novel low-dimensional materials
11:05-11:30	Sara Bals	Atomic Resolution Imaging in 3D
11:30-11:55	Joanne Etheridge	Revealing the structure of nanostructured materials using convergent electron beams
11:55-12:20	Nobuo Tanaka	Development and future directions of environmental high-voltage scanning transmission electron microscopy
12:20-13:40	Lunch Break	
13:40-14:05	Grace Burke	Environmentally-Assisted Cracking – Then and Now: Advances in Understanding Environmental Reactions in Steels
14:05-14:30	Haimei Zheng	Nanomaterials Transformations and Dynamic Phenomena at Solid-Liquid Interfaces
14:30-14:55	Peter Crozier	Oxygen Reactivity and Exchange on Oxide Nanoparticle Surfaces
14:55-15:20	Steve Pennycook	New insights into materials with the NUS ARM
15:20-15:50	Coffee Break	
15:50-16:15	Eva Olsson	Advanced In Situ Electron Microscopy of Nanostructured Energy and Quantum Devices
16:15-16:40	Eric Van Capellen	STEM strategies and achievements at Thermo Fisher Scientific
16:40-17:05	Yuichi Ikuhara	Mechanical and Chemical Dynamics of Oxide Interfaces and Surfaces
17:05-19:00	POSTER SESSION at NUS Staff Club	

TUESDAY, November 14		**Location: NUS University Hall Auditorium**
8:30-8:55	Rafal Dunin-Borkowski	Model-based reconstruction of magnetization distributions in nanoscale materials from electron-optical phase images
8:55-9:20	Martha McCartney	Electron holography of nanoscale electric and magnetic fields
9:20-9:45	Toshiaki Tanigaki	Magnetic field observations by high-voltage electron holography
9:45-10:10	Juan-Carlos Idrobo	What we Gain with Aberration-Correctors and Monochromators
10:10-10:40	Coffee Break	
10:40-11:05	Naoya Shibata	Atomic resolution differential phase contrast scanning transmission electron microscopy
11:05-11:30	Maria Varela	Sub-unit cell mapping of magnetic quantities across oxide interfaces
11:30-11:55	Xiaoqing Pan	Understanding novel domain science in multiferroic materials by advanced electron microscopy
11:55-12:20	Young-Min Kim	Multiferroic properties of BiFeO3 thin films controlled by geometrically-induced oxygen octahedral tilts
12:20-13:40	Lunch Break	
13:40-14:05	Eiji Okunishi	Investigation of delocalization in pseudo atomic column mapping by using STEM-moiré method, reconstructed with Silicon K and L electrons detected by EELS & EDS
14:05-14:30	Sergei Kalinin	Atomic Fabrication via Electron Beams
14:30-14:55	Hanfang Hao	High resolution imaging, nanostructuring and nano analytics with He and Ne Ions
14:55-15:20	Martial Duchamp	TEM imaging of 2D transition metal dichalcogenides in the 100 K to 1000 K temperature range
15:20-15:50	Coffee Break	
15:50-16:15	Peter van Aken	Effects of dopant size and octahedral distortions on novel functionalities in perovskite-based oxide heterostructures
16:15-16:40	Wu Zhou	Low voltage aberration corrected STEM for two-dimensional heterostructures
16:40-17:05	Chris Regan	Imaging RRAM switching processes
17:05-17:30	Kristian Mølhave	New Capabilities for In-situ Electron Microscopy of Liquid Processes
17:45-21:00	River Cruise and CONFERENCE DINNER	

WEDNESDAY, November 15		**Location: NUS University Hall Auditorium**
8:30-8:55	Masashi Watanabe	Validation of Multivariate Statistical Analysis on Spectrum-Imaging Datasets for Quantification
8:55-9:20	James Wittig	The Role of Electron Microscopy in the Development of High-Density Magnetic Recording Media
9:20-9:45	Tom Kelly	Seeing Every Atom in a “Large” Specimen: What will it take?
9:45-10:10	Guillermo Solórzano	Grain Boundary Diffusion–Controlled Phase Transformations in Metallic Nanomaterials
10:10-10:40	Coffee Break	
10:40-11:05	Nigel Browning	Using Sub-Sampled STEM and Inpainting to Control the Kinetics and Observation Efficiency of Dynamic Processes in Liquids
11:05-11:30	Wolfgang Jäger	Atomic resolution characterization of GaSb/GaInAs and GaSb/GaInP wafer bond interfaces for high-efficiency solar cells
11:30-12:30	Lunch Break	

Invited Talks

In situ high resolution and environmental electron microscopy studies of material reactions

R. Sinclair[1*] and A. L. Koh[1]

[1] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305-4034, USA
[*] bobsinc@stanford.edu

There has been a steady growth in the applications and breadth of *in situ* transmission electron microscopy (TEM) since the 1980's [1]. In a series of studies, we established that high resolution TEM recordings could be made in real time, *in situ* and that the atomic behavior associated with materials reactions at interfaces could be deduced (e.g. [2],[3]). Moreover, with the advent of thin film and nanotechnology, the investigation of thin and nano-scale materials became a necessity (e.g. [4]). In recent years, there has been an additional proliferation, most notably from *in situ* TEM in controlled environments such as in gases and liquids (e.g. [1], [5]), and from the application of aberration-corrected TEM (e.g. [6]).

This paper gives a short review of the application of *in situ* high resolution TEM to investigate material reactions. An overarching theme of our work has been to ensure that the *in situ* studies are truly representative of the real behavior of the material system, and we have advanced a number of guidelines to ensure this. Moreover, we have also expanded our approach to environmental material-gas reactions such as carbon nanotube (CNT) oxidation [7], and the *in situ* study of CNT field emission for high intensity X-ray sources [8]. The influence of the imaging electron beam is more important for the gaseous reactions, as it ionizes the reacting gas species, and it is necessary to develop protocols to take this into account [9]. The procedures we have adopted to do this will be carefully described [10].

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Instrumental developments for high-resolution in-situ Electron Microscopy: opportunities and limitations

M. Haider*, M. Linck and H. Müller

CEOS GmbH, Englerstr. 20, D-69126 Heidelberg, Germany
* haider@ceos-gmbh.de

The development of new components for high-resolution Electron Microscopy has pushed the achievable resolution limit to new not anticipated areas over the last two decades. The emergence of correctors to compensate the unavoidable spherical aberration has improved the attainable information limit for TEM [1] as well as for STEM [2]. However, not only the spherical aberration limits the resolution but also the chromatic aberration Cc. Hence, besides the corrector also monochromators have been developed with which the attainable information limit in TEM could be improved due to the reduced energy spread of the electron source. The other possibility to reduce the focus spread caused by Cc is the compensation of Cc by means of a Cc-corrector. However, after the development of a Cc-corrector the achieved resolution was not as high as anticipated. Detailed investigations of the source of this limited resolution at higher energies turned out that free electrons in any conductive piece next to the electron beam are causing a so-called Johnson noise [3].

Besides the limitation of the attainable resolution by any sort of noise or by higher order or residual aberrations there are also opportunities to improve the resolution by dedicated aberration correctors, eventually in combination with a monochromator. The disturbing Johnson noise can be reduced at lower energies by an optimized Cc-corrector and ray path. As a consequence, new resolution limits could be achieved with Cc-correction for the SALVE project [4].

Due to these developments of correctors and monochromators there are new opportunities of high resolution electron microscopy for in-situ applications even when more space within the objective lens is required.

U_A/kV	λ / pm	50 mrad limit		SALVE Achievements	SALVE with resp. λ
20	8.589	5.82 /nm	171.8 pm	128 pm / 139 pm	14.9 / 16.2
30	6.979	7.16 /nm	139.6 pm	108 pm / 115 pm	15.5 / 16.5
40	6.016	8.31 /nm	120.3 pm	88.5 pm / 90 pm	14.7 / 15.0
60	4.866	10.28 /nm	97.3 pm	80 pm / 83 pm	16.4 / 17.1
80	4.176	11.97 /nm	83.5 pm	69 pm / 76 pm	16.5 / 18.2

*TAB. 1. The measured information limit of the SALVE instrument at energies between 20 – 80 keV after compensation of Cs and Cc. The best result with respect to the used energy was obtained at 40 keV with an information limit to be around 15 * λ. The 2 right columns are showing the values of the best and its perpendicular direction.*

References

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Ultra-high spatial and energy resolution STEM/EELS

T.C. Lovejoy[1*], N.J. Bacon[1], A.L. Bleloch[1], N. Dellby[1], M.T. Hotz[1] and O.L. Krivanek[1,2]

[1] Nion, 11511 NE 118th St, Kirkland, WA, 98034, USA
[2] Department of Physics, Arizona State University, Tempe AZ 85287, USA
[*] lovejoy@nion.com

The ground-potential monochromator and highly stable EEL spectrometer developed by Nion are presently reaching <10 meV energy resolution EELS on a routine basis, and < 5 meV resolution appears to be just around the corner. This has extended the capabilities of the electron microscope, especially for vibrational spectroscopy [1], by allowing:

- damage-free identification of different hydrogen bonds in biological samples [2]
- vibrational spectroscopy using the non-dipole signal, with sub-nm spatial resolution [3]
- probing vibration modes at surfaces and edges of nano-objects [4]
- mapping phonon dispersion in momentum space with nm-scale spatial resolution [5]

Monochromation can also improve the spatial resolution, which is limited to

$$d_{probe(Cc)} \sim (C_c\, \delta E)^{1/2} / E^*_o{}^{3/4},$$

where C_c is the chromatic aberration coefficient, δE the energy spread and E^*_o the relativistically corrected primary energy. Two approaches to overcoming this limit, which is especially severe at low keV, are possible: correcting *Cc*, or decreasing the energy spread δE. The second approach has the advantage that it also provides superior EELS energy resolution. We have used it to attain 1 Å spatial resolution at 30 keV.

Improving the spatial resolution at low keV only becomes possible if the geometric aberrations are corrected up to about 50 mrad half-angle, which requires precise control of parasitic aberrations of 4th and 5th order, in addition to the usual full control of 2nd and 3rd order aberrations. Accordingly, the Nion aberration corrector now allows complete correction of all primary and parasitic aberrations up to $C_{5,6}$ [6]. Correcting the geometric aberrations to this extent and decreasing the energy spread from the unmonochromated value of 350 meV to around 100 meV allows 1.07 Å resolution to be reached at 30 keV, thus lowering the d/λ figure of merit to 15. The smaller energy spread also allows the chromatic "tail" of the probe to be reduced, leading to improved image signal-to-background ratios.

Nion's new EEL spectrometer provides high energy stability (instability and energy drift <10 meV / minute), and aberration correction up to about 50 mrad half-angle (measured at the sample). We have also developed a high dynamic range 2kx2k EELS camera that can detect single electrons (at 30-200 keV) as well as >200 primary electrons/ pixel without saturating, and is robust enough to measure an intense Zero Loss Peak without damage.

As we approach sub-5 meV resolution EELS, electron microscopy will enter an era of *diffraction-limited EELS*, in which the resolution of the energy spectrum will be limited by diffraction effects, and opening up the spectrometer entrance angle (while correcting the spectrometer aberrations) will lead to *better* energy resolution. The new spectrometer has been designed precisely with this new era in mind.

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Nanoswitches: TEM characterization of resistively switching oxides

J. Mayer[1,2*], M. Bornhöfft[1], H. Du[1,2], V. Migunov[2] and C.L. Jia[2,3]

[1] Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, Jülich 52425, Germany
[2] Central Facility for Electron Microscopy, RWTH Aachen University, Aachen 52074, Germany
[3.] School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[*] mayer@gfe.rwth-aachen.de

The present work aims at a comprehensive understanding of the resistive switching mechanism in both oxide and phase change materials [1,2] on the basis of the local structural and bonding information at atomistic level obtained by aberration corrected (scanning) transmission electron microscopy ((S)TEM). For this purpose, we employ the advanced TEM and STEM facilities available at the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons.

By employing aberration-corrected HRTEM and STEM, we conduct a detailed analysis of the atomistic structures of the different phases and defects, which are considered to play essential roles in the switching properties of oxides and other chalcogenides [3-5]. In our experiments, we aim at elucidating the atomistic structure of the filaments and elementary clusters which control the switching kinetics. Moreover, monochromated STEM enables us to obtain atomically resolved information on the electronic structures of the nanoscale defects and their coupling to the structural transitions [6].

Furthermore, we use the so-called fluctuation TEM technique to statistically analyse time-dependent nanodiffraction patterns. This technique makes it possible to investigate the short range and medium range order in amorphous materials and the unique crystallization kinetics of the phase change materials.

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[7] The authors acknowledge support by the German Research Foundation DFG in the framework of the Collaborative Research Centre SFB 917.

High-resolution transmission electron microscopy of electron beam-sensitive crystalline materials

D. Zhang, Y. Zhu, L. Liu, and Y. Han*

King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
* yu.han@kaust.edu.sa

High-resolution imaging of electron beam-sensitive crystalline materials is one of the most difficult applications of transmission electron microscopy (TEM). The challenges are manifold, including the acquisition of images with an extremely low beam dose, the time-constrained search for crystal zone axes, the precise alignment of successive images, and the accurate determination of the defocus value.

We reported that using a direct-detection electron-counting (DDEC) camera, it is possible to acquire useful high-resolution TEM images with electron dose as low as a few electrons per square angstrom to ensure that the intact structure was captured before damage occurred [1]. In this talk, we will present a suite of new methods that we recently developed to address the rest challenges mentioned above. Our methods advance the HRTEM of extremely beam-sensitive materials from "occasionally possible" to "routine". We demonstrate the effectiveness of our methodology by capturing atomic-resolution (~ 1.5 Å) TEM images of several metal organic frameworks (MOFs) that are generally recognized as highly sensitive to electron beams. In the case of MOF UiO-66, individual metal atomic columns, various types of surface termination, and benzene rings in the organic linkers, are clearly identified. We also successfully apply our methods to other electron beam-sensitive materials, and achieve atomic-resolution TEM imaging of the organic-inorganic hybrid perovskite $CH_3NH_3PbBr_3$ for the first time [2].

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Probing the electronic structure of solids with EELS

G.A. Botton*, E.P. Bellido, I. C. Bicket, V. Kapetanovic, H. Liu, A. Pofelski

Canadian Centre for Electron Microscopy, and Dept of Materials Science and Engineering, McMaster University, Hamilton, ON, L8S- 4M1, Canada,
* gbotton@mcmaster.ca

Electron energy loss spectroscopy (EELS) is an invaluable technique to study the detailed structure and the chemical state of materials at unprecedented spatial resolution. In today's modern electron microscopes, it is possible to tackle problems requiring the highest energy resolution to detect losses down to 70meV, so that atomic resolved spectroscopy with high spectroscopic sensitivity and resolution can be obtained. This leads to the potential of covering excitation phenomena from the mid-infrared, soft-X-rays and even hard-X-ray regime.

In this presentation, various examples of applications of electron microscopy will be given. First of all, the detection of low-loss features in plasmonic nanostructures and nanoantennas, down to the mid-infrared part of the electron energy loss spectrum, will be given, and this by directly imaging plasmon resonances down to 0.17eV and phonon resonances down to 70meV. Then we will then discuss hybridization effects demonstrating strong field enhancements between simple nanostructures, in fractal structures and in conductive oxides and nitrides. We will then demonstrate examples of detailed structural and analytical work applied in the study of battery materials to highlight how EELS can provide information on the active species and the evolution of cathode materials following electrochemical cycling [3,4]. Finally we will highlight how the near-edge structures can provide a fundamental understanding on the hybridization and bonding in different cathode materials, high-temperature superconductors [5] and information on the hole carriers distribution in highly correlated oxides [6].

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Direct imaging of channel constituents in beryl

C. Gspan[1], W. Grogger[1], H. Fitzek[1], Daniel Knez[1], G. Kothleitner[1], K. Gatterer[2], F. Hofer[1*]

[1] Institute for Electron Microscopy and Nanoanalysis, [2] Institute for Physical and Theoretical Chemistry, Graz University of Technology, 8010 Graz, Austria
[*] ferdinand.hofer@tugraz.at

Scanning transmission electron microscopy (STEM) has proven to be an indispensable method for mapping the location and identity of atoms in complex materials. However, there are only a few STEM studies available, which concentrate on channel constituents in nanoporous materials [e.g. 1]. In this paper, we try to identify the channel constituents in a natural beryl sample using STEM in combination with other analytical methods.

The crystal structure of beryl with the ideal formula $Al_2Be_3Si_6O_{18}$ (space group P6/mcc) is known since more than 90 years and has been refined several times by means of X-ray and neutron diffraction. However, the interesting point is that this structure contains channels along the c-axis, which do not have a uniform diameter, but instead consist of cavities (cages) with a diameter of around 0.5 nm, separated by "bottlenecks" (constrictions) in the plane of the silicon oxide rings with a diameter of 0.28 nm. The cavities may be filled by various minor constituents such as small molecules (e.g. H_2O, CO_2) and alkali ions. Especially, in natural beryl very complex substitutions may be observed.

The beryl sample investigated in this study shows a pale blue-green colour (aquamarine), and low concentrations of iron, water, and caesium. The findings from different methods (Raman and UV-VIS spectrometry, SEM-WDX) in combination with image simulations helped us to identify two different species present in the channels of the beryl sample. Most of the filled channels contain water molecules and only very few contain Cs atoms (see figure).

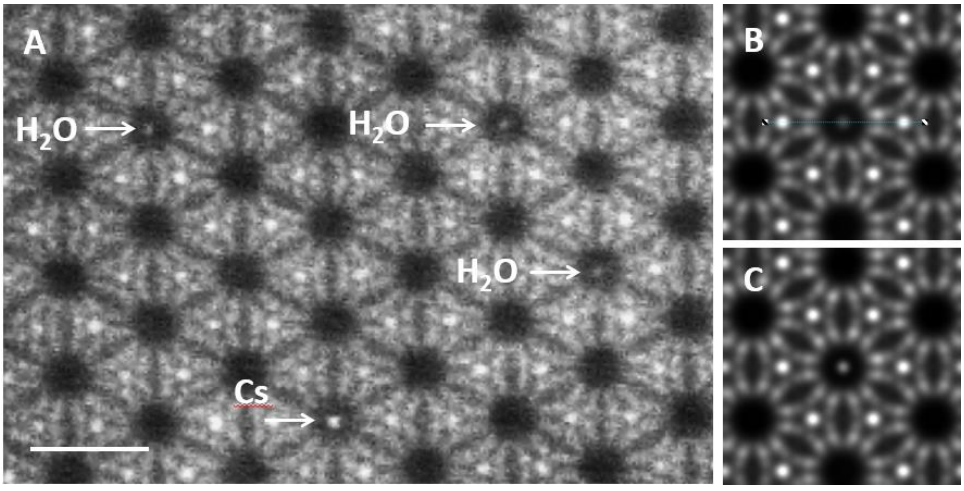

FIG. 1. STEM investigation of a pale blue-green aquamarine (beryl) viewed along the c-axis. (A) *HAADF image revealing two different channel constituents (sample thickness 36 unit cells).* (B) *HAADF simulation for 72 H_20 molecules in a channel (maximum load).* (C) *HAADF simulation for one caesium atom in a channel (scale bar = 1 nm).*

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Studying Heteroepitaxial Compound Semiconductors

David J. Smith[1*], B.D. Tracy[1], M. Lassisse[2], J. Lu[3], M.R. McCartney[1] and Y.-H. Zhang[2]

[1] Department of Physics, Arizona State University, Tempe, AZ 85287-1504, USA
[2] School of Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, 85287, USA
[3] School of Engineering for Matter, Transport and Energy, Arizona State University, Tempe, 85287, USA
[*] david.smith@asu.edu

Heteroepitaxial growth of compound semiconductors presents many challenges. In addition to preparation of the substrate surface and careful attention to the growth conditions, there are several additional obstacles when growing heterovalent structures based on two (or more) different materials. As well as lattice mismatch, which inevitably leads to strain and likely defect formation, valence mismatch and differences in thermal expansion, are further factors that can seriously impact the eventual epilayer quality. The transmission electron microscope has a wide range of imaging, diffraction and analytical techniques that can provide invaluable information about the often-competing effects of growth conditions and compositional differences. The development of aberration correction has enabled electron microscope information limits to be extended beyond the 1-Å resolution barrier, and makes it (almost) routine to achieve atomic-resolution imaging from many different types of materials. For elemental and compound semiconductor heterostructures, it is even possible to resolve the projections of individual atomic columns, often referred to as dumbbells, in the common <110> direction. Composition profiles across heterovalent interfaces, as well as bonding information at the atomic level, can also be achieved when using the probe-corrected configuration. This talk will describe and compare our recent studies of isovalent (valence-matched) II-VI/II-VI and III-V/III-V structures such as ZnTe/CdTe and InSb/GaSb, and heterovalent (valence-mismatched) II-VI/III-V structures such as ZnSe/GaAs and CdTe/ InSb, using aberration-corrected electron microscopy.

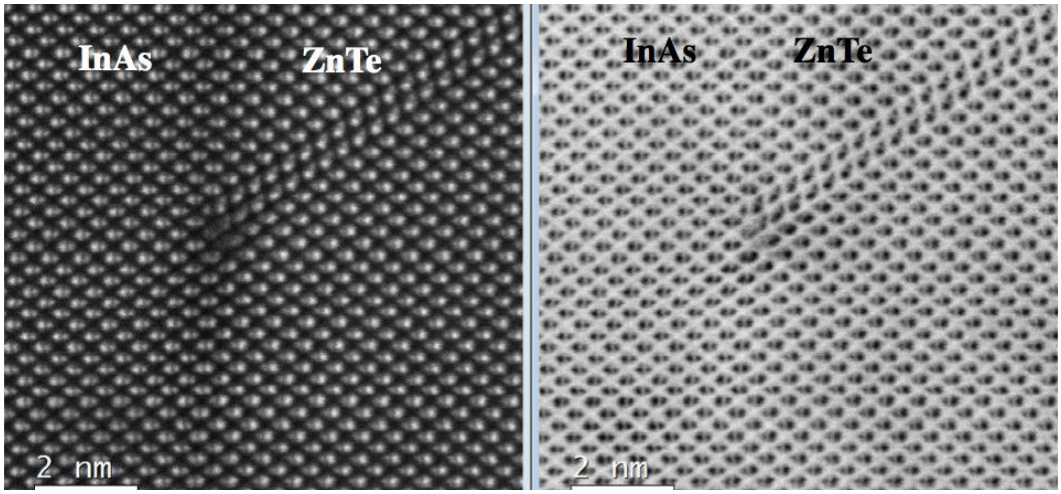

FIG. 1. AC-STEM images showing stacking fault originating at heterovalent ZnTe/InAs (001) interface: (a) HAADF (90~170mrad); (b) large-angle BF (0~22mrad).

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[1] Part of this work was supported by AFOSR Grant FA9550-15-1-019.

XEDS Applied to Soft-Hard/Matter Measurements at the Nanoscale in the Next Generation AEM

Nestor J. Zaluzec*

Photon Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
* Zaluzec@aaem.amc.anl.gov

The evolving state of detector technologies and geometries in electron-optical instruments is providing motivation to revisit the challenge of using x-ray energy dispersive spectroscopy (XEDS) for investigations of not only near atomic level characterization (under channeling conditions) in crystalline materials, but also studies of non-crystalline and soft-matter. Increasing the solid angle and drift compensation has afforded the possibility of analysis of low dose rate analysis in many systems, both in-vacuo as well as using in-situ gas/liquid e-Cells. Figures 1 and 2 present a hyperspectral image of copper and zinc accumulation in a thin organic membrane which under older systems is untenable. Optimizing signal both with respect to minimum detectable mass (MDM) and minimum mass fraction (MMF) is a parallel consideration and experimental measurements (figure 3) indicate a wide range of operating conditions can be realized, and may be optimized depending upon the desired measurement.

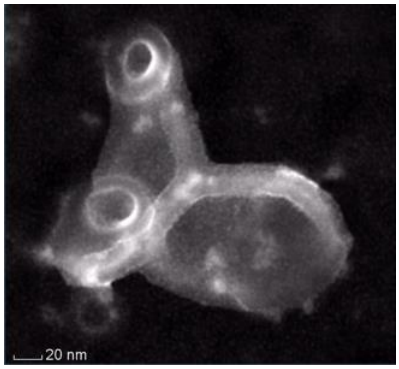

Figure 1.) HAADF of folded structure and deposits in an organic membrane.

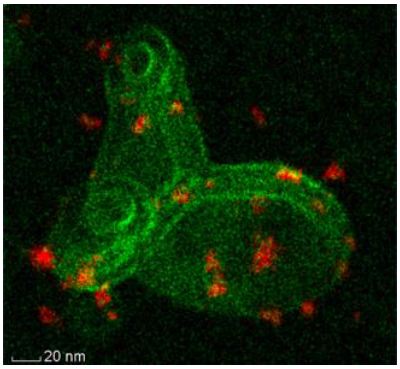

Figure 2.) Hyperspectral Image of Zinc and Copper distributions

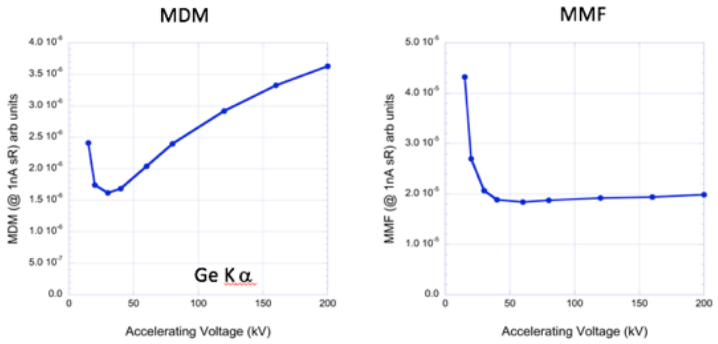

Figure 3: Experimental variation in MDM and MMF for Ge XEDS analysis as a function of incident beam energy.

References

[1] This work was supported by the Photon Science Division and Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. Some of the measurements in this study were conducted using instruments in the Center for Nanoscale Materials at Argonne National Laboratory as well as at the Thermo-Fisher - FEI NanoPort in Eindhoven, NL.

Low-voltage STEM-EELS characterization of novel low-dimensional materials

K. Suenaga[1*]

[1] Advanced Industrial Science and Technology (AIST), AIST Central 5, 305-8565, Tsukuba, Japan
[*] suenaga.kazu@gmail.com

Properties of low-dimensional materials are largely influenced by its structural imperfections, such as defects, impurities, edges or boundaries. Hence, analytical technique at the single-atom level is becoming crucial to fully understand their physical/chemical performance. In my presentation, single atom spectroscopy by means of electron energy-loss spectroscopy (EELS) will be shown to discriminate individual atoms in low-dimensional materials at their interrupted periodicities. It is emphasized here that information of the bonding/electronic states has become accessible for single atoms through the EELS fine-structure analysis [1] as well as the spin state [2, 3]. Large variations of local electronic properties of 1D and 2D materials with different atomic coordinates will be investigated [4, 5].

I will also show some examples for the optical-range electron-spectroscopy of low-dimensional materials [6, 7, 8]. Differences between EELS and optical absorption will be discussed for surface materials in diluted systems [9].

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Atomic Resolution Imaging in 3D

S. Bals[1]

[1] EMAT-University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
[*] sara.bals@uantwerpen.be

New developments in the field of transmission electron microscopy (TEM) enable one to characterize nanomaterials at the atomic scale, not only structural, but also from chemical and electronic point of view. However, one should never forget that all these techniques only provide a two-dimensional (2D) projection of a three-dimensional (3D) object. To overcome this problem, electron tomography has been used in an increasing number of studies over the last decennium. Nevertheless, it is still not straightforward to push the resolution below the nanoscale in 3D. This relies on the combination of state-of-the-art electron microscopes and advanced computational procedures to transform the 2D images into a 3D reconstruction.

One possibility to perform electron tomography with atomic resolution is by applying reconstruction algorithms based on compressive sensing [1,2]. The methodology was applied to HAADF-STEM images acquired from defect-free Au nanorods. Going further is the aim to measure lattice strain in 3D. We therefore investigated Au nanodecahedra consisting of five segments bound by {111} twin boundaries. We compared strain investigations using 2D projection images with 3D measurements based on high resolution electron tomography reconstructions [3]. High resolution electron tomography was recently also applied to determine an unknown crystal structure. A combination of diffraction tomography and high resolution tomography in real space enabled us to investigate the distribution of Cu vacancies in $Cu_{1.5\pm x}Te$ nanocrystals. By using the outcome of these experiments as an input for first-principle calculations, the influence of these vacancies on the optical properties of the nanocrystals was determined [4].

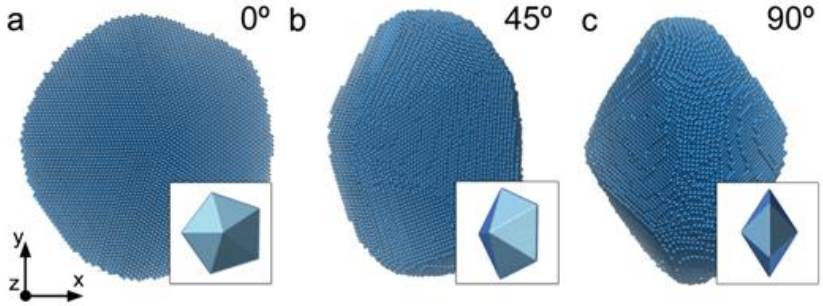

FIG. 1. 3D visualizations of the reconstruction showing the atomic lattice of a Au nanodecahedron.

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Revealing the structure of nanostructured materials using convergent electron beams

J. Etheridge[1,2*]

[1] Monash Centre for Electron Microscopy, Monash University, VIC 3800, Australia.
[2] Dept of Materials Science and Engineering, Monash University, VIC 3800, Australia.
[*] joanne.etheridge@monash.edu

Convergent beam electron diffraction (CBED) patterns are rich with information about the arrangement and bonding of atoms within a specimen. Furthermore, the converged electron probe can be tuned in size from the nanometre down to the atomic scale allowing a small and selected volume of specimen to be isolated and analysed. CBED patterns provide a momentum space map of the multiple electron scattering processes that arise as the electron wave field traverses the specimen. By interrogating key features in this pattern, different types of specimen information can be gleaned [1,2]. This talk will discuss some recent developments in the theory and application of CBED, as well as the imaging mode it underpins; scanning transmission electron microscopy (STEM). It will illustrate these with various applications to nanostructured materials, including plasmonic nanoparticles; functional perovskites and semiconductor systems [3-6].

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Development and future directions of environmental high-voltage scanning transmission electron microscopy

Nobuo Tanaka* and Shigeo Arai

Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University, Nagoya, 464-8603, Japan.
* a41263a@nucc.cc.nagoya-u.ac.jp or * n-tanaka@nagoya-u.jp

Nagoya University has been one of pioneering institutes for in-situ and environmental transmission electron microscopy /diffraction since world-war II[1]. Since then, various kinds of in-situ electron microscopy were conducted such as that for dislocation movement by Imura et al.[2]. In the 1990s, our in-situ TEM observation has arrived at an atomic resolution for studies of growth of atomic clusters of metals[3] and photocatalytic behavior of TiO_2 by using a UV illumination system[4].

As a fruit of these accumulated researches, Nagoya University has developed a unique environmental high-voltage (S)TEM equipped with an open-type environmental cell and STEM-EELS capability[5]. The present talk covers the results on catalytic reactions of porous gold with CO gas[6], hydrogen brittleness of composite alloys and semiconductors[7], diesel catalysis[8], and platinum reaction of carbon nanotubes (CNT)[9,10], as well as 3D observation of biological whole cells such as yeast cells[11]. As a future direction, "in-place observation" with controlled beams is essentially important. Development of a HVEM holder with non-exposure to air for battery materials is also presented in the talk[12].

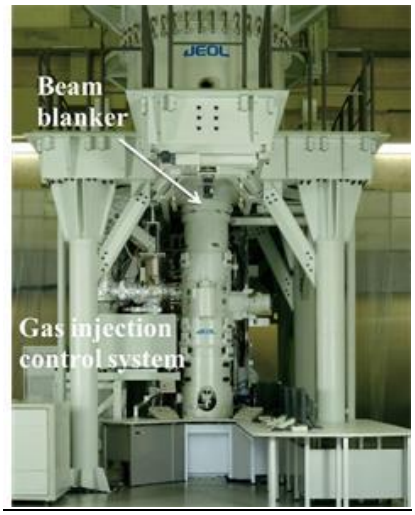

FIG. 1: Front view of an environmental HV-(S)TEM in Nagoya University

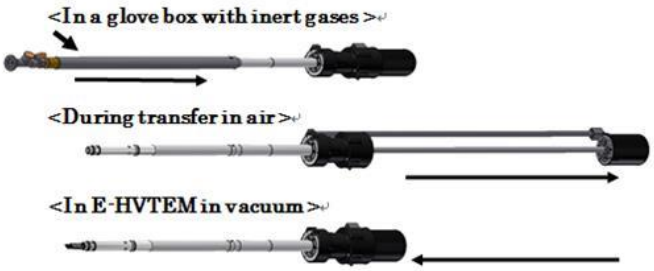

FIG. 2: Structures of a HV-(S)TEM holder with non-exposure to air.

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Environmentally-Assisted Cracking – Then and Now: Advances in Understanding Environmental Reactions in Steels

M. G. Burke*

Materials Performance Centre, University of Manchester
* M.G.Burke@manchester.ac.uk

In situ TEM research has a long history, dating back over 50 years, but it became more prominent with the development of high voltage transmission electron microscopes (late 1960's-1970's). In particular, studies dealing with materials degradation, oxidation, and reduction were possible with the development of specific stages and environmental cells.[1] These impressive studies relied on "thick" TEM specimens in order to simulate bulk environmental interactions and minimize reactions that would be dominated by surface effects. Research on the environmental degradation of various metals and alloys included studies on hydrogen embrittlement[3], stress corrosion cracking, and oxidation/reduction of Fe[4]. With the advent of liquid in situ environmental cells, it is now possible to explore nanoscale reactions as well as measure electrochemical properties in the analytical TEM.

This presentation will discuss developments in the application of this technique to explore environmentally-assisted cracking, corrosion and associated environment-material interactions in conventional alloys, and how this technique is generating new information to aid our understanding of materials degradation.

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Nanomaterials Transformations and Dynamic Phenomena at Solid-Liquid Interfaces

Haimei Zheng[1,2*]

[1] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720
[2] Department of Materials Science and Engineering, University of California, Berkeley, CA 94720
[*] hmzheng@lbl.gov

An understanding and ultimately controlling of materials dynamic processes at liquid-solution interfaces is important for a variety of applications including solution synthesis of materials, energy conversion and storage devices, materials corrosion and others. We study materials dynamic phenomena at the atomic level by developing and applying liquid environmental cell transmission electron microscopy (TEM). In this talk, I will show the revealing of nanocrystal growth in solution, including noble metal nanoparticles, transition metal oxide formation and shape evolution with liquid cell TEM. Assisted with Density Functional Theory calculation, the energetic barriers for materials transformations and ligand effects are achieved, which allows a depth understanding of organic ligand mediated nanocrystal growth and transformations in solution. In the end, I will also show using our development of electrochemical cells and sample stage, we have been able to observe a series of electrochemical phenomena at the electrode-electrolyte interfaces that is critical to the understanding of electrochemical devices, i.e., batteries.

Oxygen Reactivity and Exchange on Oxide Nanoparticle Surfaces

E.L. Lawrence[1], Q. Liu[1], T. Boland[1], B.D.A. Levin[1], P. Rez[2] and P.A. Crozier[1]*

[1] School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, USA
[2] Department of Physics, Arizona State University, Tempe, Arizona, USA
* crozier@asu.edu

Oxygen exchange at surfaces and interfaces is a critical functionality impacting many energy conversion technologies. In catalysis, lattice oxygen is involved in oxidation and reduction in the well-known Mars van Krevelen process. On fuel cells, the oxygen exchange reaction at the cathode is often the rate limiting step because it involves a difficult 4 electron transfer process. The exchange reaction is favored on non-stoichiometric oxides because it involves the creation and annihilation of oxygen vacancies at the surface. Understanding atomic level factors, that regulate oxygen exchange on oxide surfaces, remains a significant challenge. *In situ* aberration-corrected TEM imaging and spectroscopy is a potentially powerful tool to explore local structural and compositional motifs associated with oxygen reactivity. Here we discuss several examples where imaging and spectroscopy provides key information on the oxygen exchange process.

Undesirable carbon deposition (coking) onto catalyst during reforming of hydrocarbons to CO and H_2 (syngas) can be suppressed via lattice oxygen exchange. Carbon deposition may be reduced in a suitably designed bifunctional catalyst possessing two classes of active sites: one site for syngas formation and one site for oxidation of carbonaceous intermediates. Metal nanoparticles on a reducible oxide, such as Ni/CeO_2, may show the desired bifunctionality with metal sites for generating syngas and interfacial sites to oxidize carbon species. Using a combination of *in situ* imaging and spectroscopy we show that the amount of carbon deposition is inversely proportional to the oxygen vacancy concentration at the metal/ceramic interface. Differences in the amount of carbon deposited during reforming of ethane and ethylene are discussed in terms of thermodynamic and kinetic factors.

At thermodynamic equilibrium, a reducible oxide is constantly exchanging oxygen with the gas phase at a rate that depends on the vacancy formation energy, which varies with surface defects and facets. Oxygen vacancies will cause displacements in the neighboring metal cations. Figure 1 shows an image of a stepped (111) surface of a CeO_2 nanocrystal. The cation position at the step edges in Figure 1 is significantly blurred suggesting displacements on the order of 0.2 – 0.3 Å. This is consistent with cation displacements predicted by molecular dynamics simulations in the presence of high oxygen vacancy concentrations. Significant differences are observed between surfaces of CeO_2 and TiO_2. The effect of changes in partial pressure of oxygen and water vapor on the surface dynamics is also discussed.

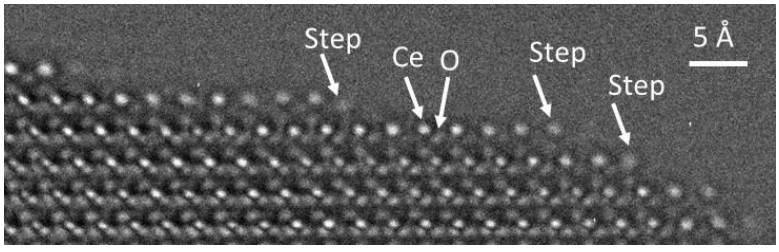

FIG. 1. Negative C_s image of stepped (111) surface on CeO_2 nanoparticle showing variation in cation contrast at step edges cause by enhanced oxygen exchange.

Acknowledgments
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New insights into materials with the NUS ARM

S.J. Pennycook,* X. Zhao, J. Dan, F. Tian, P.K. Gogol, H. Wu, M. Li, C. Tang, C. Li.

National University of Singapore, Department of Materials Science and Engineering, Block EA #07-24, 9 Engineering Drive 1, Singapore 117575
* steve.pennycook@nus.edu.sg

The National University of Singapore installed a JEOL ARM200F last year, incorporating a cold field emission gun, ASCOR aberration corrector, UHR pole piece, Gatan Quantum ER spectrometer, OneView camera and Oxford Aztec EDS system. It is installed within a JEOL environmentally controlled room and shows sub-Ångstrom information transfer even at 40 kV accelerating voltage (see Fig. 1). Examples will be shown of new edge structures in nanoporous MoS_2 with good catalytic properties [1], the atom-by-atom fabrication of monolayer Mo membranes via beam induced sputtering, and beam-induced healing of holes.

In piezoelectrics, precise mapping of atomic displacements reveals a hierarchical nanodomain structure as the origin of excellent properties [2,3]. Similarly, in thermoelectrics, a hierarchical structure ranging from point defects through nanoscale and microscale precipitates is observed in a high-performance material with lattice thermal conductivity approaching the theoretical minimum.

The ASCOR corrector can provide probe semi-angles up to 60 mrad which allows depth resolution at the nm-scale. In a TiO_2 film grown on $LaAlO_3$, La is seen to have preferentially diffused along stacking fault intersections originating at an interface step.

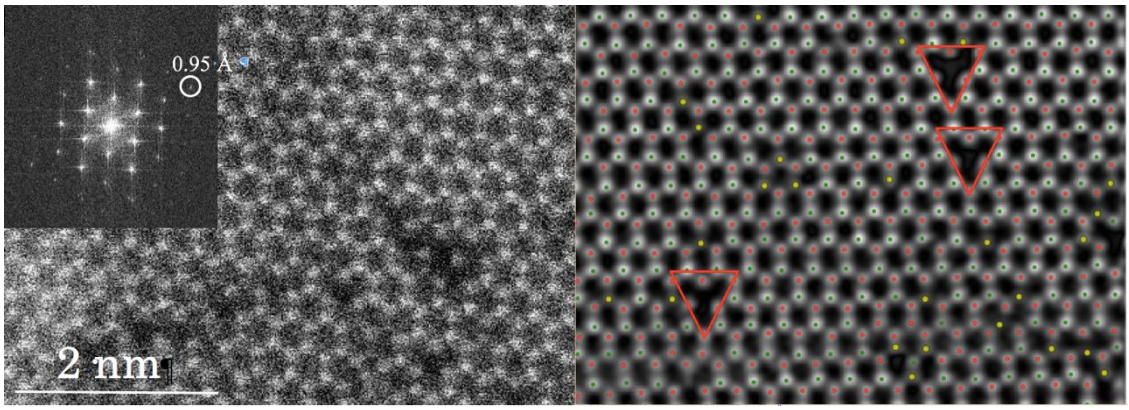

FIG. 1. Left: STEM image of $MoSe_2$ obtained at 40 kV showing information transfer to 0.95 Å (inset fast Fourier transform). Right: A filtered image (not the same sample) showing identification of Mo (red), Se_2 (green), Se (yellow, single vacancy), and Se divacancies (red triangles). Data taken on a JEOL ARM200F with ASCOR corrector at 40 kV, courtesy Xiaoxu Zhao and Jiadong Dan.

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Advanced In Situ Electron Microscopy of Nanostructured Energy and Quantum Devices

E. Olsson*

Department of Physics, Chalmers University of Technology, SE- 412 96 Gothenburg, Sweden
* eva.olsson@chalmers.se

In situ electron microscopy enables the direct observation and correlation between material structure and properties on small scales reaching the atomic level. Examples of important mechanisms that can be studied are those of transport properties of charges, heat, liquids and particles in complex structures and also of effects induced by light, mechanical strain and temperature changes.

The direct correlation on the small scale involving individual interfaces, defects and atoms provides access to new information about which microstructural constituents that are active in determining the material properties on the macro, micro, nano and atomic scale. New aspects of material properties and mechanisms not obvious from measurements on the macro scale can also be revealed due to the high spatial resolution. The knowledge is crucial for not only the understanding of the mechanisms that are involved but also for the design or materials and devices with tailored properties. This talk will address transport properties, electric field and charge dynamics in nanostructured materials [1-7]. Different aspects of specimen geometries and electron beam effects for the correlation between structure and properties will also be discussed.

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STEM strategies and achievements at Thermo Fisher Scientific

E. Van Cappellen[1*], I. Lazić[2], E. Bosch[2], P. Tiemeijer[2], S. Lazar[2], B. Freitag[2] and E. Yücelen[2]

[1] Thermo Fisher Scientific Hillsboro, Hillsboro OR 97124, USA
[2] Thermo Fisher Scientific Acht, 5600 KA, Eindhoven, The Netherlands
[*] eric.van.cappellen@fei.com

Annular Dark Field (ADF) is the technique of choice for HR-STEM imaging because of some well-established properties. "Bright" Field (BF) techniques have a clear advantage when it comes to signal-to-noise and light element sensitivity but BF imaging saw little acceptance until Annular Bright Field (ABF) was introduced [1].

The above "conventional" techniques use disc and annulus shaped STEM detectors but the new trends are to change these geometries. The simplest non-conventional geometry is a segmented disc or annulus and the most complex one is a pixelated detector for so-called 4D-STEM. The most promising technique using segmented detectors is iDPC or integrated Differential Phase Contrast [2] and the many desirable properties of iDPC will be discussed.

When the entire diffraction pattern is recorded in every image pixel many more STEM applications become feasible [3-5]. Thermo Fisher Scientific and Cornell University have entered a strategic collaboration to develop and productize a dedicated Pixel Array Detector for 4D-STEM, the EMPAD [6].

Last but not least the latest developments in monochromated STEM will be presented. They include improved resolution at low accelerating voltages and accessibility to very low-energy loss imaging. Phonon imaging requires very high energy resolution and an example acquired on MgO cubes (similar to [7]) also demonstrates the need for sufficient current even at these extreme energy resolutions (Fig. 2).

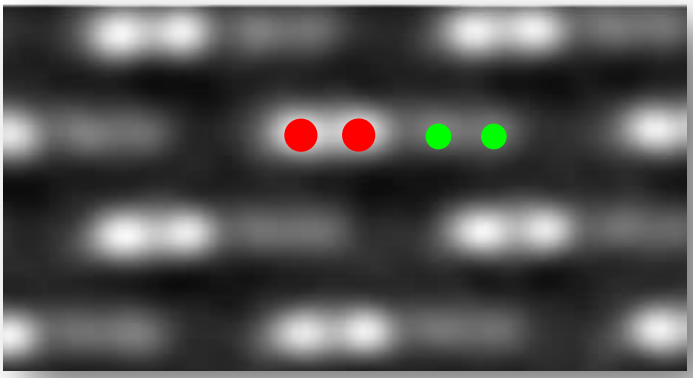

FIG. 1: iDPC of Ga<112> at 300kV. Both the bright Ga dots (red) and the darker N dots (green) are separated by 63pm.

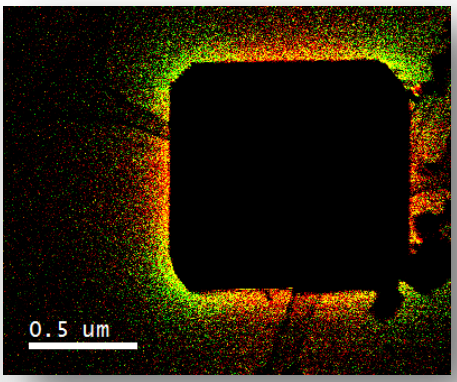

FIG. 2: Phonon imaging on MgO. The corner modes are at 70meV and the face modes at 77meV

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Mechanical and Chemical Dynamics of Oxide Interfaces and Surfaces

Yuichi Ikuhara[1,2,3*]

[1] Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan
[2] Nanostructures Res. Lab., Japan Fine Ceramics Center, Nagoya, 456-8587, Japan
[3] WPI-AIMR Research Center, Tohoku University, Sendai, 980-8577, Japan
[*] ikuhara@sigma.t.u-tokyo.ac.jp

So far, many experimental investigations have been tried to understand the dislocation-grain boundary interaction in materials, but these experiments were mostly carried out statically, and the dynamic behavior is still not well understood yet. It has been known that several oxide crystals can be plastically deformed even at R.T. by dislocation slip like metals. In this study, the in-situ nanoindentation experiments were conducted for $SrTiO_3$ single crystal and its bicrystals inside TEM. For bicrystal experiments, various types of GBs including CSL (Coincidence Site Lattice) GBs and low angle tilt and twist GBs were prepared. It was found that whether dislocations can penetrate across GBs depends on the grain boundary characters (GB orientation and plane). Various interface phenomena such as dislocation pile-up at GBs, jog formation, jog-drag motion were dynamically observed. The dislocation-GB interaction and its dependence on the GB characters will be discussed in detail.

The properties of lithium ion battery (LIB) cathodes strongly depend on the diffusion of lithium ions during charge/discharge process. Then, direct visualization of lithium site is required to understand the mechanism of the diffusion of lithium ions. In this study, aberration corrected STEM were applied to directly observe the {010} surface, which corresponded to perpendicular to the 1-D diffusion orientation, of the olivine Li_xFePO_4. The morphology of the interface between Li-rich and Li-poor phases of Li_xFePO_4 after chemical delithiation were observed with atomic resolution at fit intervals during half a year. It was found that orientation of boundary layers at the $FePO_4/Li_{2/3}FePO_4$ interface gradually changed from lower index planes to higher index planes. This indicates that intermediate phase plays an important role in healing crystal cracking by allowing the interface to remain coherent so that Li ions can diffuse back into regions depleted during delithiation. The mechanism of the lithiation/delithiation from and to the surface will be discussed based on the observation results.

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Model-based reconstruction of magnetization distributions in nanoscale materials from electron-optical phase images

J. Caron[1], P. Diehle[1], A. Kovács[1], J. Ungermann[2], and R. E. Dunin-Borkowski[1*]

[1] Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52425 Jülich, Germany
[2] Institute for Energy and Climate Research, Forschungszentrum Jülich, 52425 Jülich, Germany
[*] rdb@fz-juelich.de

We have developed a model-based approach to magnetic vector field tomography, which involves using an iterative reconstruction algorithm to recover the three-dimensional magnetization distribution in a specimen from a series of magnetic phase images recorded using off-axis electron holography as a function of sample tilt angle. The advantage of using a model-based approach is that each trial solution satisfies known physical laws. The initially ill-posed problem is replaced by a least-squares minimization problem. First order Tikhonov regularization is applied and a mask is used to localize magnetized objects. All measures are combined into a cost function, whose minimization is facilitated by conjugate gradient methods. Diagnostic tools are used to assess the quality of the reconstruction result. Sources of magnetization outside the field of view are accounted for by introducing buffer pixels. A confidence array is used to exclude other identifiable artefacts from the reconstruction. Figure 1 shows a reconstruction of a magnetised disc that supports a vortex state generated from two tilt series of simulated magnetic phase images. A central slice along the x axis is also shown. The reconstruction is in very good agreement with the original magnetisation distribution. Encouraging experimental results have been obtained from magnetic nanoparticles and magnetic skyrmions [1].

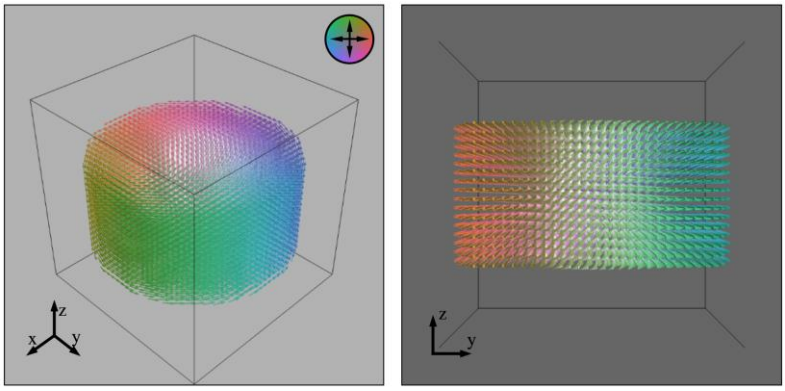

FIG. 1 Reconstructed magnetisation distribution of a vortex state in the xy plane calculated from two tilt series of simulated magnetic phase images about the x and y axes for a maximum tilt angle of ±90° and an angular sampling of 5. The colour wheel encodes the magnetisation direction in the xy plane, while white arrows point in the positive z direction.

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[1] The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ ERC grant agreement number 320832. We are grateful to Z.-A. Li, M. Riese, M. Farle, N. Kiselev and S. Blügel for ongoing cooperations and contributions to this work.

Electron holography of nanoscale electric and magnetic fields

Lin Zhou[1], Zhaofeng Gan[2], Kai He[3], David J. Smith[4] and Martha R. McCartney[4*]

[1] Ames Laboratory, Ames, IA 50014, USA
[2] Intel Corporation, Hillsboro, OR 97124, USA
[3] Northwestern University, Chicago, IL, 60208 USA
[4] Department of Physics, Arizona State University, Tempe, AZ 85287, USA
[*] molly.mccartney@asu.edu

Off-axis electron holography in the transmission electron microscope provides a unique and powerful approach to visualizing electric and magnetic fields within materials with resolutions approaching the nanometer scale. The ability to image phase shifts at medium resolution opens up a wide field of interesting and important materials problems. In this work, the technique has been successfully used to quantify electrostatic and magnetic fields in and around deep-submicron devices and patterned nanomagnets. An important extension of this work has involved *in situ* application of magnetic fields to image local magnetic response during hysteresis loops. Applications include asymmetric pinning of domain walls at notches in nanowires. Electrostatic field examples include imaging of electrostatic phase shifts at quantum dots to allow for quantification of charge capture, measurement of piezoelectric fields and 2-dimensional electron gas densities. In situ biasing examples include doped Ge-Si nanowires allows for analysis of activation of dopants and lithiation of Ge nanowires.

As an example, we measured charge distribution during lithium ion insertion into a Ge nanowire (NW) under dynamic operating conditions [1]. Figure 1(a) is a hologram recorded while lithiation was taking place, while Figure 1(b) shows the corresponding phase image. Profile measurements, combined with simulations, enabled the Li component of the NW to be estimated and the amount of trapped charge to be quantified.

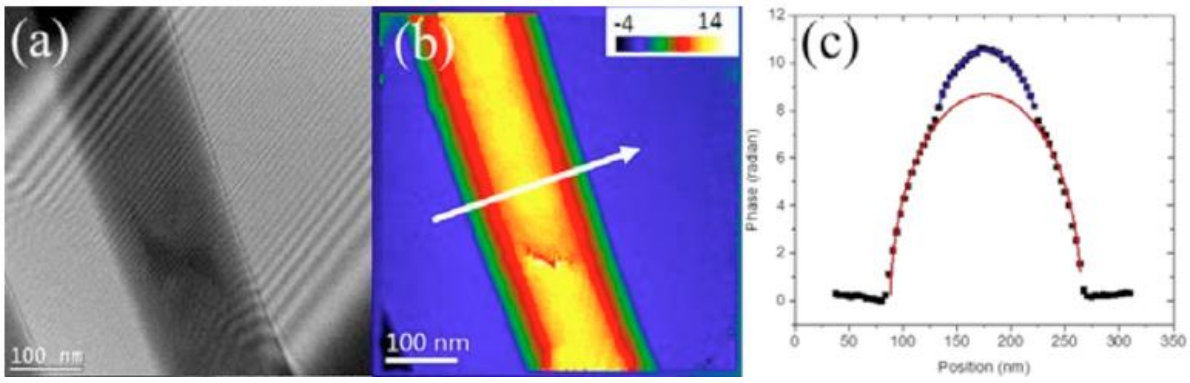

FIG. 1(a) hologram of Ge/Li $_x$ Ge core/shell NW structure during lithiation; (b) reconstructed phase image; (c) phase profile(dotted) and simulation (solid) along indicated arrow in (b).

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Magnetic field observations by high-voltage electron holography

T. Tanigaki*, T. Akashi, A. Sugawara, and H. Shinada

Hitachi, Ltd., 350-0395 Hatoyama, Japan
* toshiaki.tanigaki.mv@hitachi.com

Electron holography is unique technique to observe electrostatic potential and magnetic fields inside and around samples. The quest for the ultimate resolution through continuous development of the holography electron microscopes led to the development of aberration corrected 1.2-MV holography electron microscope [1].

The high penetration power of a high energy electron wave is crucial to observing magnetic structures, which exist only in thick samples. It is particularly crucial in 3D observation, which requires a series of sample observations with the sample increasingly tilted so that the projected sample thickness increases with the tilt angle. As one example of this, magnetic vortex cores confined in stacked ferromagnetic (Fe) discs were observed three-dimensionally by vector-field electron tomography using a 1.0-MV holography electron microscope [2].

The spatial resolution in magnetic field observation has been limited by the large aberrations of the objective lens for setups in which the sample is placed in a field-free position, which is necessary to determine the inherent magnetic structures without modification by the magnetic field of the objective lens. Although the aberration corrector has brought about a sub-nanometer resolution for field-free observation, high-resolution magnetic field observation is still hampered by technical difficulties in improving magnetic phase sensitivity and separating electrostatic and magnetic phases at high spatial resolution. To overcome these difficulties, we developed a pulse magnetizing system to automatically acquire a set of holograms with opposite magnetization states [3]. This system reverses the magnetization in the sample without changing the sample geometry, enabling high spatial resolution to be obtained in magnetic field observations.

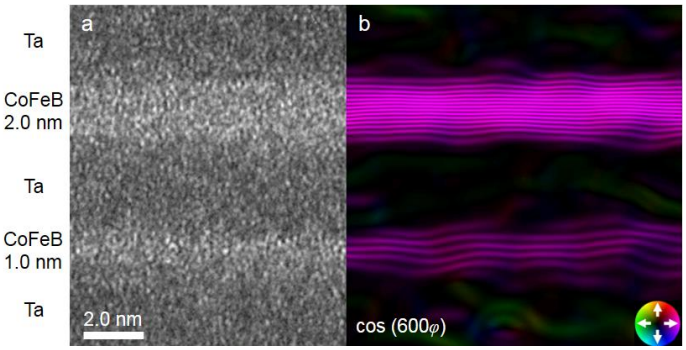

FIG. 1. Magnetic field in CoFeB/Ta multilayer. (A) *TEM image.* (B) *Magnetic induction.*

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What we Gain with Aberration-Correctors and Monochromators

Juan-Carlos Idrobo[1*]

[1] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[*] idrobojc@ornl.gov

Until very recently, the goal of aberration-correction in STEM has been to produce the possible smallest electron probes. The reasoning is that smaller probes result in images and spectra with better spatial resolutions. However, it has been recently argued on theoretical grounds that in some cases it is desirable to have an atomic-size electron probe with customized aberrations [1]. In this talk I will discuss how one can use aberrated electron probes to detect magnetic ordering by observing a dichroic signal in the fine structure of an L-edge in a transition metal element for the case of the antiferromagnetic LaMnAsO [2].

I will also present our current efforts to study local lattice vibrations using electron energy-loss spectroscopy (EELS). The physical basis for EELS is that a high energy electron beam in a (S)TEM will interact with the electrons or phonons inside the sample, exciting them from lower to higher energy states, while losing a corresponding amount of energy. However, the opposite interaction is also possible: the fast electron can gain energy from a sample that is initially in a higher energy state, albeit with an exponentially smaller probability that depends on the temperature of the sample. Here, I will show that we can directly measure the local temperature of boron nitride flakes in the nano-environment using monochromated electron beams [3]. Finally, I will present examples of how we can detect the bonding configuration of individual atoms in monolayer graphene and even discriminate between different hydrogen isotopes in water nano drops encapsulated in monolayers of boron nitride [4].

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Atomic resolution differential phase contrast scanning transmission electron microscopy

Naoya Shibata[1,2 *]

[1] Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan
[2] Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan
[*] shibata@sigma.t.u-tokyo.ac.jp

Due to the recent rapid progresses in segmented/pixelated detector developments combined with the state-of-the-art aberration correction technologies, atomic-resolution differential phase contrast (DPC) imaging in scanning transmission electron microscopy (STEM) is now becoming possible. It has been shown that atomic resolution DPC STEM can visualize atomic electric field, the field between positively charged atomic nucleus and negatively charged surrounding electron clouds [1-3]. Figure 1 show simultaneous annular dark field (ADF) image, electric field vector color map and electric field strength map of $SrTiO_3$ crystal observed from [001] direction, constructed from atomic resolution DPC STEM [3]. Here, we use high-speed segmented type detector combined with a center of mass detection method [4]. Comparing with the simultaneous ADF image, disks of rotating color contrast are seen at each atomic column position in the electric field vector map. The direction of rotating color contrast is the same in all the atomic columns irrespective of the atomic species, visualizing that the (projected) atomic electric field points outward from the center of the atomic columns. In this talk, current status and prospects for atomic-resolution DPC STEM will be discussed.

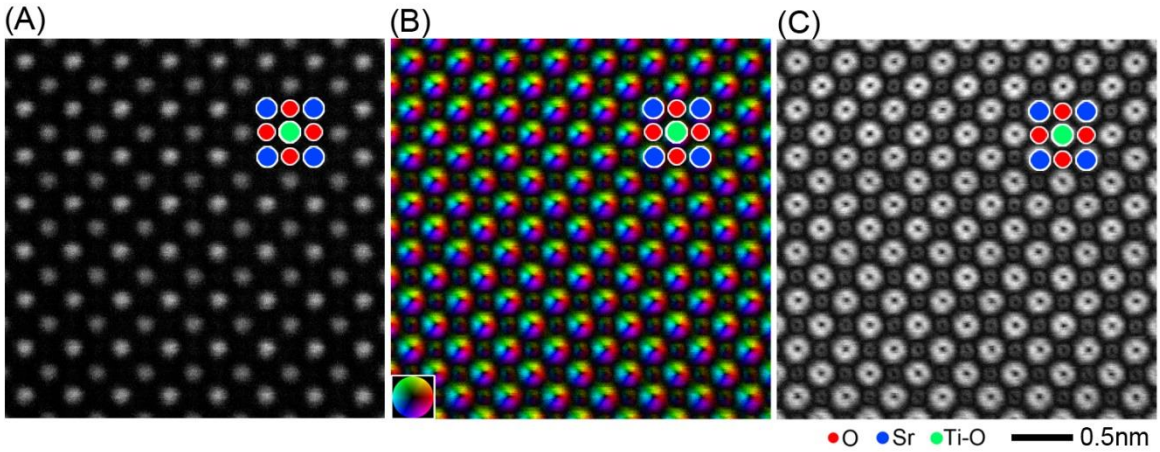

FIG. 1. (A) ADF STEM image. (B) Projected electric field vector color map and (C) electric field strength map constructed from the segmented detector STEM images [3]. The inset color wheel indicates how color and shade denote the electric field orientation and strength in the vector color map.

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Sub-unit cell mapping of magnetic quantities across oxide interfaces

J. Grandal[1], J. I. Beltran[1], J. Tornos[2], F. J. Rodriguez[1], G. Sanchez-Santolino[2], C. Leon[1,3], M. C. Muñoz[2], J. Santamaria[1,3] and M. Varela[1,3,4*]

[1] GFMC, Dept. de Fisica de Materiales, Universidad Complutense de Madrid, 28040 Madrid, Spain.
[2] Instituto de Ciencia de Materiales de Madrid. Cantoblanco 28049, Madrid. Spain.
[3] Instituto de Magnetismo Aplicado, Universidad Complutense de Madrid, 28040 Madrid, Spain.
[4] Instituto Pluridisciplinar, Universidad Complutense de Madrid, 28040 Madrid, Spain.
[*] mvarela@ucm.es

Magnetic oxides with perovskite structure exhibiting colossal magnetoresistance are very relevant systems from the point of view of both physical properties and technological relevance. This talk will discuss local measurements of electronic and magnetic properties of ferromagnetic manganite $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) epitaxial ultrathin films grown by high-pressure O_2 sputtering on single crystal $SrTiO_3$ (STO) substrates. We will combine the use of advanced electron microscopy techniques such as electron energy-loss spectroscopy (EELS) in the aberration-corrected scanning transmission electron microscope (STEM) with density-functional calculations to study local structural distortions and electronic phenomena associated with interfacial magnetism. Atomic resolution images exhibit an increase of the out-of-plane lattice parameter at the LSMO/STO interface plane, pointing to a local reconstruction of the charge density and, hence, physical properties. We use energy-loss magnetic chiral dichroism (EMCD) [1,2], a technique directly sensitive to the local magnetic moment, to track magnetic quantities across the interface with sub-unit cell resolution. The dichroic signal at both the Mn $L_{2,3}$ and the Ti $L_{2,3}$ edges is enhanced near the interface, pointing to a local increase of the Mn and Ti magnetic moments. These results agree will be discussed in the light of density-functional theory simulations including the presence of interfacial oxygen vacancies, which enhance charge transfer processes along with antiferromagnetic coupling between Ti and Mn atoms.

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Understanding novel domain science in multiferroic materials by advanced electron microscopy

Xiaoqing Pan[1*]

[1] Department of Chemical Engineering and Materials Science and Department of Physics and Astronomy, University of California – Irvine, Irvine, CA
[*] xiaoqinp@uci.edu

As advances in transmission electron microscopy (TEM) have enabled the determination of the three-dimensional structure and local properties of materials with the sub-angstrom resolution, the recent development of *in situ* TEM techniques allows one to follow the dynamic response of nanostructured materials to applied fields. In this talk, I will present our recent TEM studies of the polarization ordering and dynamic domain switching behaviors of ferroelectric/multiferroic thin films. It was found that the charged domain walls can be created or erased by applying a bias, and the resistance of the local film strongly depends on the characteristics of the charged domain walls. It will also be show that the surface monolayer of conducting oxide can induce a giant spontaneous polarization in ultrathin multiferroelectric films and that a peculiar rumpled nanodomain structure, which is in analog to morphotropic phase boundaries (MPB), is formed. Finally, it will be demonstrated that small defects in ferroelectric thin films can act as nano-building-blocks for the emergence of novel topological states of polarization ordering, namely, polarization vortex/anivortex/hedgehog/antihedgehog nanodomain arrays. I will also give an overview of new research opportunities concerning domains in ferroelectric/multiferroic materials.

Multiferroic properties of $BiFeO_3$ thin films controlled by geometrically-induced oxygen octahedral tilts

Young-Min Kim[1,2*], Sung Su Lee[3], and Ji Young Jo[3]

[1] Department of Energy Science, Sungkyunkwan University, Suwon 16419, Korea
[2] Center for Integrated Nanostructure Physics, Institute for Basic Science, Suwon 16419, Korea
[3] School of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 61005, Korea
[*] youngmk@skku.edu

Oxygen octahedral tilts (OOT) of perovskite transition metal oxides are known to be linked to electrical and/or magnetic behaviors, since the tilt angle associates with both the length and angle of the bond between B-site cation and oxygen via overlap of the *d* orbitals and localized charge carriers. Control of the OOT angle can thus allow us to engineer electrical and magnetic behaviors and to examine the complex relationships between the oxygen octahedral structure and multi-functionalities of perovskite oxides [1]. In this study, we present an innovative strategy to control simultaneous magnetic and ferroic orders in a multiferroic $BiFeO_3$ thin film by artificially tuning octahedral tilt patterns at the heterointerface (see Fig. 1). We show that changing the octahedral structural coherency in bottom monoclinic/tetragonal $SrRuO_3$ platform layers can metastasize through the stoichiometric $BiFeO_3$ thin film over 25 nm, resulting in controllable multiferroic phases.

This is the first demonstration of octahedra-derived multiferroic properties that can be stabilized in a thin film form without the help of complex chemical modifications recently reported by Pitcher et al. [2] and Mandal et al. [3]. The complex interplay between octahedral tilts and polar/magnetic orders is examined by advanced STEM, synchrotron X-ray scattering, and magnetic measurements, revealing that the tilt symmetry is critical to tailoring the multiferroicity. Our approach provides a new platform to manipulate lattice-coupled ferroic order parameters including the dramatic enhancement of ferroelectricity and the realization of unprecedented magnetization in a thin film form.

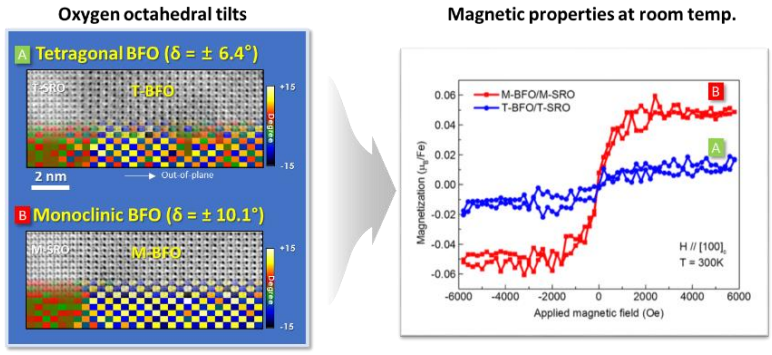

FIG. 1. Change of oxygen octahedral tilt in multiferroic BFO thin films can simultaneously tune magnetic and ferroic orders, providing a facile strategy for wide range of multifunctional nanodevice applications that exploit octahedral-derived properties.

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Investigation of delocalization in pseudo atomic column mapping by using STEM-moiré method, reconstructed with Silicon K and L electrons detected by EELS & EDS

E. Okunishi[1*] and Y. Kondo[1]

[1] JEOL Ltd., 3-1-2 Musashino, Akishima, Tokyo, 196-8558, Japan.
[*] okunishi@jeol.co.jp

The characteristics of the atomic column elemental mapping, such as spatial resolution or quantitative capability, have been requested to clarify experimentally, since it is important to estimate its advantages and disadvantages of the method [1]. For example, delocalization of analysis, which is one of the important physical parameter, is determined by accelerating voltage of a primary electron and an energy at the absorption edge of a sample. For measurement of such physical parameter, it is ideal to perform under the condition with no sample damage, because the damage makes displacement of atoms, resulting in a large measurement error.

With the 2D STEM moiré method, which is already succeeded to display the pseudo atomic column elemental map, under low dose condition [2, 3] was used to examine the delocalization of elemental signal on the pseudo atomic column elemental maps.

Figures 1(a~e) shows the simultaneously obtained pseudo atomic column maps of Si (110) with HAADF signal (a), $L_{2,3}$ and K signal by EELS (b, c) and K signal by EDS(d). The pseudo dumbbell by moiré method in Si (110) sample is clearly shown as in HAADF image. The peaks in elemental maps also show the atom sites of Si atoms. Figure 1(f) shows the intensity profiles of Si K by EDS, $L_{2,3}$ electrons by EELS and HAADF along a yellow region shown in Figures 1(a~d), after background subtraction and normalization. Comparing these intensity profiles, those show little difference. The profiles of HAADF and Si-K(EELS and EDS) have consistent shape. Profile of Si-L(EELS) has wider peaks than another profiles (see dips of dumbbell). We suppose that it is due to delocalization effect. We are obtaining similar results from thinner and thicker region as well.

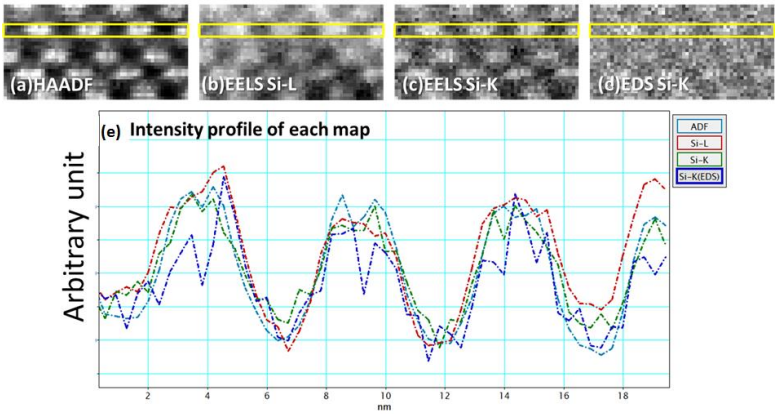

FIG. 1(a~d). simultaneously obtained pseudo moiré atomic column maps of Si. Fig. 1(e) show the profiles of signals from yellow region in Fig. 1 (a-d).
Used microscope was JEM-ARM200F with cold FEG, working at 200 kV. The sample thickness was estimated to be ≈ 250 nm.

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Atomic Fabrication via Electron Beams

Sergei V. Kalinin,[1,2] Ondrej Dyck,[1,2] Albina Borisevich,[1,3] and Stephen Jesse[1,2]

[1] The Institute for Functional Imaging of Materials
[2] The Center for Nanophase Materials Sciences and
[3] Materials Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[*] sergei2@ornl.gov

Fabrication of atomic scale structures remains the ultimate, and yet not achieved, goal of nanotechnology. The reigning paradigms are scanning probe microscopy (SPM) and synthesis. SPM assembly dates back to seminal experiments by Don Eigler, who demonstrated single atom manipulation and writing. However, stability and throughput remain issues, and only in the last decade synergy of STM and surface chemistry was used to make several-qubit devices. The molecular machines approach harnesses the power of modeling and synthetic chemistry to build individual functional blocks, yet strategies for structural assembly remain uncertain.

In this presentation, I discuss the research activity coordinated by the Institute for Functional Imaging of Materials (IFIM) towards the third paradigm—the use of atomically focussed beam of scanning transmission electron microscope to control and direct matter on atomic scales. Traditionally, STEMs are perceived only as imaging tools, and any beam induced modifications are undesirable beam damage. In the last five years, our team and several groups worldwide demonstrated that beam induced modifications can be more precise. We have demonstrated ordering of oxygen vacancies, single defect formation in 2D materials, and beam induced migration of single interstitials in diamond like lattices. What is remarkable is that these changes often involve one atom or small group of atoms, and can be monitored real time with atomic resolution. This fulfills two out of three requirements for atomic fabrication. I will introduce several examples of beam-induced fabrication on atomic level, and demonstrate how beam control, rapid image analytics, and image- and ptychography based feedback allows for controlling matter on atomic level. As relevant examples, I will demonstrate controlled motion of Si atoms on graphene and creation of the dimers, trimers and tetramers of Si atoms and moving of dopant and phase fronts in bulk Si and $SrTiO_3$.

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High resolution imaging, nanostructuring and nano analytics with He and Ne Ions

Jens Peter Hermann Gnauck[1], Hanfang Hao[1*]

[1] Carl Zeiss Microscopy, D-73447 Oberkochen, Germany
[*] hanfang.hao@zeiss.com

The Helium Ion Microscope has been described as an impact technology offering new insights into the structure and function of nanomaterials. Combining a high brightness Gas Field Ion Source (GFIS) with unique sample interaction dynamics, the helium ion microscope provides images offering unique contrast and complementary information to existing charged particle imaging instruments such as the SEM and TEM. Formed by a single atom at the emitter tip, the helium probe can be focused to below 0.25nm offering the highest recorded resolution for secondary electron images. The small interaction volume between the helium beam and the sample also results in images with stunning surface detail.

Besides imaging, the helium ion beam can be used for fabricating nanostructures at the sub-10nm length scale. Researchers have used the helium ion beam for exposing resist and features as small as 4nm have been reported. The main advantage of helium ion lithography over electron beam lithography is the minimal proximity effect. The helium ion beam has also been used for deposition and etching in conjunction with appropriate chemistries. Helium induced deposition results in higher quality deposits than with Ga-FIB or EBID (Electron Beam Induced Deposition). Finally, the helium and neon ion beams can be used for direct sputtering of different materials. Patterning of graphene has resulted in 5nm wide nanoribbons and 3.5nm holes in silicon nitride membranes have been demonstrated.

By analyzing the sputtered material by means of SIMS the Helium Ion microscope can be transferred into a powerful nano analytical system. First evaluation of SIMS mapping performed with a Ne Ion beam shows lateral resolution lower than 20nm.

Combining the unique properties of the Gas Field Ion Source (GFIS), brightness and spot size together with the SIMS capabilities of a sector filed mass spectrometer result in a unique imaging and analytical tool.

TEM imaging of 2D transition metal dichalcogenides in the 100 K to 1000 K temperature range

M. Duchamp[1], K. Bogaert[2], M. Spina[3], P. Machain[1], E. Tyukalova[1], S. Garaj[3,4], S. Gradecak[2], C. B. Boothroyd[1]

[1] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798.
[2] Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts, USA.
[3] Centre for Advanced 2D Materials, National University of Singapore, Singapore.
[4] Department of Physics, National University of Singapore, Singapore.
[*] mduchamp@ntu.edu.sg

Two-dimensional transition metal dichalcogenides (TMDs) possess a variety of properties that make them attractive for applications in electronic, energy and sensing applications. Imaging 2D TMD structures using a transmission electron microscope (TEM) allows the local atomic configuration to be determined at the temperature of observation, usually room temperature. The introduction of MEMS-based chips on newly available TEM holders allows atomic resolution imaging over the temperature range from 100 K to 1000 K. Similar to conventional semiconductors, the electronic properties of 2D TMDs strongly depends on the temperature. The electronic properties may be tuned owing to the temperature dependence of the bandgap energy as well as by the presence of phase transitions. Also interesting are modifications of the structure upon annealing at high temperatures.

We present TEM observations of various 2D TMD structures both in diffraction and real space across the 100 K to 1000 K temperature range using a unique liquid nitrogen holder based on MEMS chip technology which is stable enough for high resolution imaging at any temperature up to 1000 K. Fig. 1 shows examples of STEM imaging after high temperature annealing of an alloy of 2D $Mo_xW_{1-x}S_2$ structures (Left) and edge reconstruction of WSe_2 (Right).

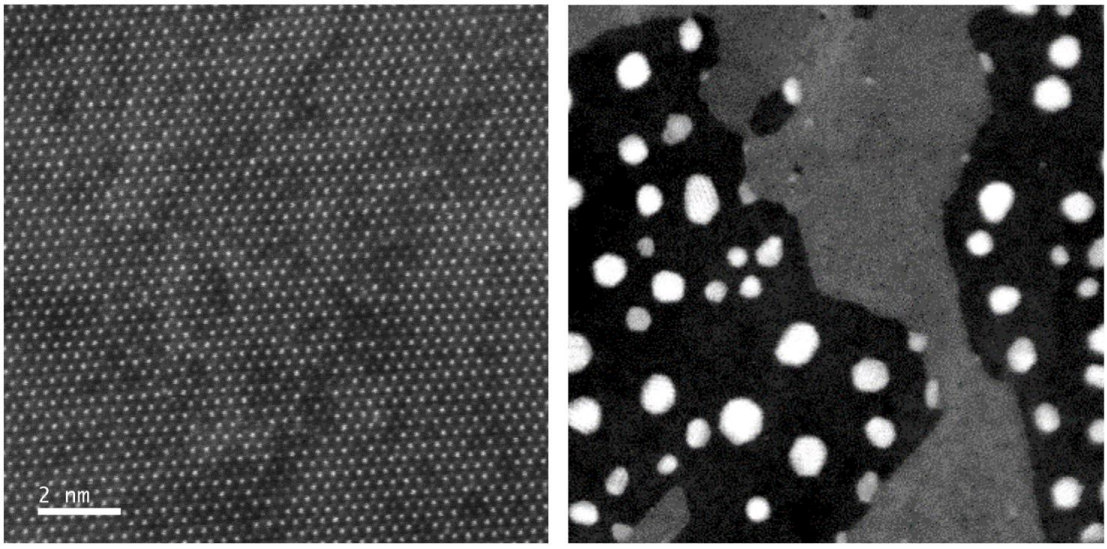

FIG. 1. Left: STEM image of $Mo_xW_{1-x}S_2$ after annealing at 650 °C. Right: STEM image of WSe_2 showing edge reconstruction after annealing at 700 °C. Both images were taken at 80 kV.

Effects of dopant size and octahedral distortions on novel functionalities in perovskite-based oxide heterostructures

Y.E. Suyolcu[1], Y. Wang[1], W. Sigle[1], F. Baiutti[1], A. Al-Temimy[1], G. Gregori[1], G. Cristiani[1], G. Logvenov[1], J. Maier[1], and P.A. van Aken[1*]

[1] Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
[*] p.vanaken@fkf.mpg.de

Tuning the octahedral network represents a promising route for achieving new properties and functionalities in perovskite-based oxide heterostructures. Among the range of complex interactions, especially at the interfaces of epitaxial functional oxide systems, contributing to the occurrence of intriguing effects, a predominant role is played by the local structural parameters. One of the interface-mediated phenomena occurring in these complex oxides is the Jahn–Teller effect, where octahedral distortions occur at the epitaxial interfaces.

In this study, atomic layer-by-layer oxide molecular beam epitaxy grown lanthanum cuprate-based bilayers (consisting of a metallic (M) and an insulating phase (I)), in which high-temperature superconductivity arises as a consequence of interface effects, are considered. In assessing the role of the dopant size and distribution on the local crystal structure and chemistry, and on the interface functionalities, different dopants (Ca^{2+}, Sr^{2+} and, Ba^{2+}) are employed in the M-phase, and the M–I bilayers are investigated by complementary techniques, including analytical spherical-aberration-corrected scanning transmission electron microscopy [1].

Here we report on the interrelation between the cationic size mismatch between dopant (M^{2+}) and host La^{3+} ions and the local structure, and we discuss the impact of the dopant distribution on the structural (CuO_6 octahedra elongation) local properties. A series of exciting outcomes are found: (i) the average out-of-plane lattice parameter of the bilayers is linearly dependent on the dopant ion size, (ii) each dopant redistributes at the interface with a characteristic diffusion length, and (iii) the superconducting properties are highly dependent on the dopant of choice. A clear correlation between dopant size and local lattice deformations is highlighted. Moreover, a relation between the nature of superconductivity (bulk vs interface) and Jahn–Teller distortions of the anionic sublattice is suggested [2].

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Low voltage aberration corrected STEM for two-dimensional heterostructures

Wu Zhou[1,2,*], Yu-Yang Zhang[1,3], Jianyi Chen[4], Dongdong Li[1], Jiadong Zhou[5], Zheng Liu[5], Matthew F. Chisholm[2], Sokrates T. Pantelides[3,1], Kian Ping Loh[4]

[1] School of Physical Sciences and CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, Beijing, China.
[2] Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA.
[3] Department of Physics and Astronomy and Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, TN, USA.
[4] Department of Chemistry and Centre for Advanced 2D Materials, National University of Singapore, Singapore.
[5] School of Materials Science and Engineering, Nanyang Technological University, Singapore.
[*] wuzhou@ucas.ac.cn

Aberration-corrected scanning transmission electron microscopy (STEM) operated at low accelerating voltage can now provide real space imaging and spectroscopy analysis at the atomic scale with single atom sensitivity. This opens new opportunities for quantitative study of the structure and chemistry at the interface of two dimensional (2D) heterostructures. Such studies, especially when combined with first-principles calculations, serve as an important step to correlate the interface structure with their local properties, unveil the atomic growth mechanism for new quantum-structures, and help to create new functionalities in these 2D materials via controlled growth.

Using low-voltage aberration corrected STEM imaging, we presented a systematic study of lateral 2D semiconductor heterostructures with and without lattice mismatch, where quantitative STEM imaging can be applied to perform atom-by-atom chemical mapping and strain analysis at the interfaces. We show that for 2D lateral heterostructures where the two monolayer components have similar crystal structure and negligible lattice mismatch, such as WS_2/MoS_2 or $WSe_2/MoSe_2$, lateral epitaxial growth can lead to atomically abrupt interface [1]. In contrast, strain relaxation at lateral interfaces with lattice mismatch often lead to misfit dislocation arrays. We demonstrate that such misfit dislocations can induce the formation and growth of sub-2-nm quantum-well arrays in semiconductor monolayers, driven by dislocation climb [2]. Such misfit-dislocation-driven growth can be applied to different combinations of 2D monolayers with lattice mismatch, paving the way to a wide range of 2D quantum-well superlattices with controllable band alignment and nanoscale width.

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Imaging RRAM switching processes

William A. Hubbard[1], Jared Lodico[1], Toyanath Joshi[2], Matthew Mecklenburg[3], Brian Zutter[1], Pavel Borisov[2], and David Lederman[2,4], B. C. Regan [1*]

[1] Department of Physics & Astronomy and California NanoSystems Institute, University of California, Los Angeles, CA 90095, USA
[2] Department of Physics and Astronomy, West Virginia University, Morgantown, WV 26506, USA
[3] Center for Electron Microscopy and Microanalysis, University of Southern California, Los Angeles, CA, USA
[4] Department of Physics, University of California, Santa Cruz, CA 95064, USA
[*] regan@physics.ucla.edu

Resistive random access memory (RRAM) is an emerging technology with the potential to revolutionize data storage for electronic computing. However, poor understanding of the basic physics underpinning this technology is impeding its widespread implementation. Using devices designed specifically for electron microscopy, we have imaged RRAM switching processes in situ [1]. In some cases the switching mechanisms involve gross atomic transport, which can be seen with standard scanning transmission electron microscopy (STEM) techniques. In others cases the switching mechanism involves atomic motion that is too subtle to observe directly, but can be revealed with STEM imaging techniques that are sensitive to conductivity and temperature changes.

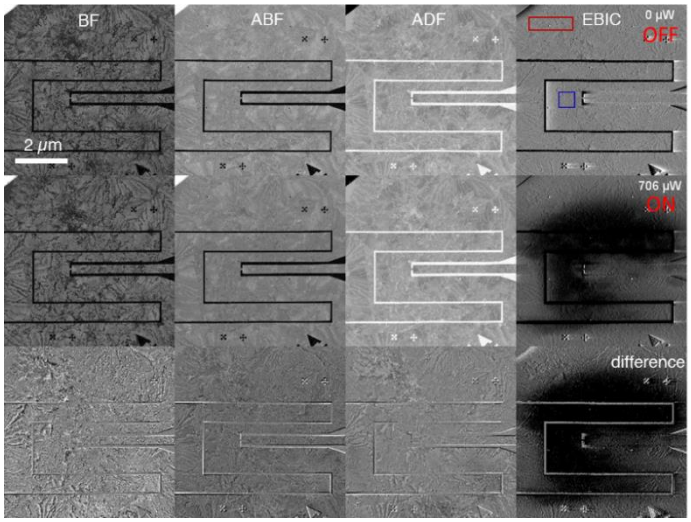

FIG. 1. The first three columns, left to right, show bright-field, annular bright-field, and annular dark-field STEM images, while the right column shows electron-beam induced current (EBIC) images of a device designed to test an NbO_2 film. The upper row shows the device at room temperature, the middle row shows the device with its heater (entering from the left) energized, and the lower row shows the difference between the two. The thermally-induced changes to the film's conductivity, which are not evident in the standard STEM images, are obvious in the EBIC images.

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New Capabilities for In-situ Electron Microscopy of Liquid Processes

Kristian Mølhave[1*]

[1] DTU-Nanotech, Dept. of Micro and Nanotechnology, Technical University of Denmark (DTU), www.nanotech.dtu.dk/mowin
[*] kristian.molhave@nanotech.dtu.dk

We are developing novel techniques allowing real-time high resolution imaging of nanoscale processes by in-situ TEM and SEM using custom built microchip based systems.

Studies with our microchip-based systems under controlled conditions often combined with correlated electrical measurements provide a deeper understanding of a variety of nanoscale processes. We develop custom built TEM [1] and SEM [2] liquid cell systems that have unique capabilities such as nanochannel based [3] microfluidic chips [4].

Work in progress quantifies radiolytic processes, and fundamental reactions such as nanoparticle synthesis [5], electrochemical reactions with dendritic growth in TEM [6] and SEM that can be compared to finite element simulations [7].

Using our nanochannel systems, we are developing liquid phase holographic imaging [8] and flow phenomena, and with our electrochemical systems we are studying diffusion, electrokinetic effects.

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Validation of Multivariate Statistical Analysis on Spectrum-Imaging Datasets for Quantification

M. Watanabe[1*] and K. Ishizuka[2]

[1] Dept of Materials Science and Engineering, Lehigh University, Bethlehem. PA, USA
[2] HREM Research Inc., Higashimatsuyama, Saitama, 355-0055, Japan
[*] masashi.watanabe@lehigh.edu

In combination with the latest hardware such as aberration-corrected scanning transmission electron microscopes (STEMs) and high-speed detectors, the advances in the recent software developments allow us to acquire large-scale spectrum imaging (SI) datasets via electron energy-loss spectrometry (EELS) and X-ray energy dispersive spectrometry (XEDS). Although the trend to acquire large-scale datasets is desired, it is more challenging to deal with (or even to analyse) the large-scale datasets. For examples, extraction of unknown features and estimation of dominant trends which are just initial steps of data analysis toward quantification are challenging enough. Multivariate statistical analysis (MSA) is one of efficient approaches to analyse the large-scale datasets in terms of feature identification and extraction [1, 2]. Since a use of MSA is relatively straightforward, various MSA approaches have been applied to SI datasets as data-mining and noise-reduction tools [e.g. 3]. Despite that the MSA approach is very efficient and useful, it may create unexpected artifacts especially in higher noise conditions [4]. Since these artifacts might mislead results, it is essential to explore the sensitivity and the validation of the MSA approach. In this study, the validation of MSA is evaluated in a quantitative manner by using simulated SI datasets. Then, procedures to improve the MSA especially fir quantification will be proposed.

In order to evaluate the MSA validation, X-ray spectra and EELS spectra were simulated using NIST Desktop Spectrum Analyzer package [5] and Gatan EELS Advisor, respectively. In the simulation, the acquisition time and the beam current were set as typical values for atomic resolution analysis in aberration-corrected STEMs. Once spectra were simulated, SI datasets were synthesized by adding a different spectrum with slightly modified composition and Poisson noise was applied to the synthesized SI datasets. Then, the MSA sensitivity was evaluated by performing MSA on the datasets. Through the evaluation of the MSA validation, it was found that the PCA reconstruction for denoising may modify absolute signals when the signal variation is in the random noise level or below.

There are two approaches to improve the MSA sensitivity: (1) reduction of random noise and (2) enhancement of true variations. The former requires modifications in experimental conditions (higher currents and longer acquisitions). Conversely, the latter can be achieved by MSA analysis to divided small segments within a SI dataset, which is now implemented as localPCA. Advantages of the localPCA approach will be discussed.

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The Role of Electron Microscopy in the Development of High-Density Magnetic Recording Media

James E. Wittig[1*], James Bentley[2], Lawrence F. Allard[3]

[1] Materials Science and Engineering, Vanderbilt University, Nashville, TN 37235, USA
[2] Microscopy and Microanalytical Sciences, PO Box 7103, Oak Ridge, TN 37831, USA.
[3] Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6376, USA
[*] j.wittig@vanderbilt.edu

The history of hard-disk drive magnetic data storage began in 1956 with the IBM Random Access Method of Accounting and Control (RAMAC) system. This RAMAC system required fifty 24 in. (61 cm) diameter disks to store a grand total of 5 Mbytes (an areal density of 2 kbits/in^2). Sixty years later, the areal data density of commercially available magnetic storage devices has increased by over 400 million times with areal densities now greater than 800 Gbits/in^2. Although more sensitive read-back heads have also contributed to this increase in areal density, equally important are the improvements in the magnetron-sputtered magnetic recording thin-film media.

Advances in magnetic recording media have relied on the structure-processing-property relationships derived from using electron microscopy methods such as high-resolution imaging (HRTEM), electron diffraction, energy-filtered imaging (EFTEM), spectrum imaging with energy-dispersive spectroscopy (EDS) and electron energy-loss spectroscopy (EELS), and Z-STEM imaging with high-angle annular dark field (HAADF). The media have evolved from Longitudinal Magnetic Recording (LMR) on CoCrPt-based alloys, to the current Perpendicular Magnetic Recording (PMR) CoPt granular media that have grain boundary oxides for magnetic decoupling (figure 1), with the future likely to be Heat Assisted Magnetic Recording (HAMR) media, which will use high magnetocrystalline anisotropy materials such as $L1_0$ ordered FePt (figure 2). Examples from over 20 years of magnetic media characterization will elucidate the essential role of electron microscopy in the development of high-density magnetic data storage with emphasis on the future FePt HAMR media.

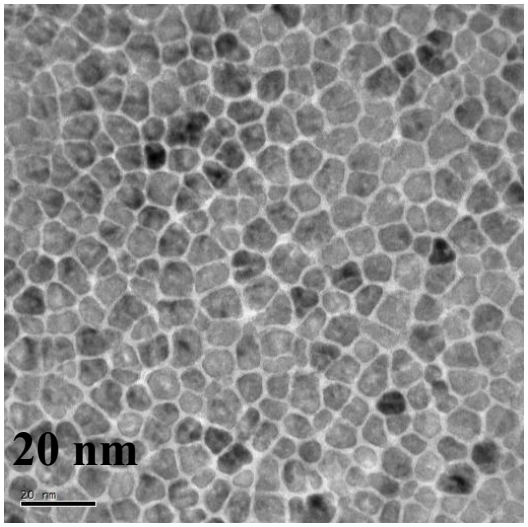

Figure 1 - Perpendicular Magnetic Recording (PMR) CoPt-oxide granular media.

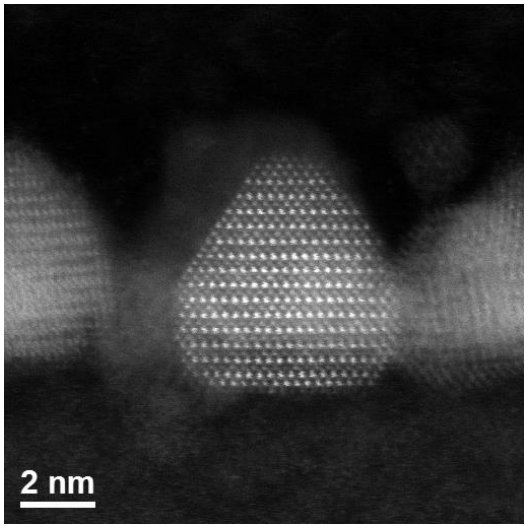

Figure 2 – Z-STEM image of $L1_0$ FePt HAMR media.

Seeing Every Atom in a "Large" Specimen: What will it take?

Thomas F. Kelly[1*]

[1] CAMECA Instruments, Inc., 5470 Nobel Drive, Madison, WI 53711 USA
[*] thomas.kelly@ametek.com

There has been interest in real space imaging of atoms in their three-dimensional locations for many decades. It has yet to be achieved except for small samples ($< 10^5$ atoms) of pure or binary alloys. In the general case, we wish to record $>10^8$ atoms in complex alloys.

There are three microscopic techniques that can resolve atoms in real space: atom probe field ion microscopy, transmission electron microscopy (TEM), and scanning probe microscopy (SPM). None of these however can image and identify every atom in large volumes in three-dimensions for arbitrary collections of atoms. The history of resolving atoms will be briefly reviewed and the prospects for imaging every atom will be considered. There may be pathways for atom probe tomography or electron microscopy to achieve this feat on their own [1] but a more likely scenario is that atom probe and TEM or SPM coupled together can get the job done [1]. There will need to be new detector technology developed as well. Each of these tasks are actively under development and we can foresee combined instruments soon that record the position and identity of every atom in complex materials for billion atom volumes. Furthermore, analytical information such as electron energy loss spectroscopy and energy dispersive x-ray spectroscopy can be integrated into these data structures for a more complete picture of the specimen [2]. Plans for achieving these goals in the next five years will be described [3].

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[3] There are several active efforts to build a combined atom probe and TEM. Project Tomo is part of the Ernst Ruska 2.0 project at Forschungszentrum Jülich with Rafal Dunin-Borkowski, Joachim Mayer, Dierk Raabe, and Max Haider. Project Laplace at the Max Planck Institute fur Eisenforschungs Düsseldorf with Dierk Raabe, Baptiste Gault, Gerhard Dehm, Christina Scheu. Previously, Simon P. Ringer, Michael K. Miller, and Krishna Rajan, Ondrej Krivanek and Nikklas Dellby were involved in the ATOM Project in the USA. Brian Gorman, David Dierks, Christoph Koch, Wouter van den Broek, and Hamish Fraser have helped with fruitful discussions and developments in LEAP-STEM. Robert McDermott and Joseph Suttle have been developing a superconducting detector. There are numerous colleagues at CAMECA including Jeff Shepard, Ty Prosa, Ed Oltman, Brian Geiser, and David Larson who have contributed also.

Grain Boundary Diffusion–Controlled Phase Transformations in Metallic Nanomaterials

Guillermo Solórzano[1*]

[1] Department of Chemical and Materials Engineering, PUC-Rio, Rio de Janeiro, Brazil
[*] guilsol@puc-rio.br

Grain boundary diffusion–controlled transformations are examined. Under this category we consider discontinuous precipitation (DP), discontinuous coarsening (DC) discontinuous dissolution (DD) and diffusion induced grain boundary migration (DIGM) phenomena. We briefly describe first the discontinuous mode of precipitation (DP) in metallic polycrystalline systems where, upon aging heat treatments, supersaturated solid solutions decomposes by the action of moving grain boundaries, acting as fast diffusion paths for solute atoms redistribution, leaving behind a depleted matrix and a lamellar or rod precipitate product growing in a cooperative fashion. From a fundamental point of view, these are among the most intriguing solid-solid transformations: their full analysis involves consideration of interacting friction, capillary and chemical forces all focused on a moving grain boundary. In this regard, discontinuous transformations products differ from those controlled by volume (lattice) diffusion, most of which can be modeled, at least to first order, on the basis of a local equilibrium hypothesis. In contrast, the non-equilibrium aspects of discontinuous transformation are central to its description. DIGM as an isolated event or as precursor for DP in some metallic system is also discussed. From the experimental point of view, through analysis in different alloy systems, we have concluded that the high resolution dedicated STEM, in its several modes of operation, is capable of yielding information of value in increasing our understanding of solid-sate transformations. In particular, the microanalysis capabilities allows the determination of diffusion data for individual moving grain boundaries and measure the residual super saturation within depleted lamellae in a DP product or in the de-alloyed region left by DIGM. That is the chemical energy stored in the material, besides the interfacial and strain energy stored at the precipitate/matrix interfaces in DP products..

We extend the analysis of the above described phenomena taking place in alloy nanoparticles and in nano-scale grain size consolidated polycrystalline material where the resulting interface multiplication in the (desired) transformation product can consume the entire matrix.

From the practical point of view, DP in structural materials has been considered as deleterious to mechanical properties. However, starting materials with high super saturation and properly engineering microstructure could develop DP and exhibit interesting physical properties. In particular, the effect on transport properties in some nano-scale grain size magnetic systems is demonstrated: while an adequate DP volume fraction generates a giant magneto resistance GMR behavior, DC annihilates this behavior.

Using Sub-Sampled STEM and Inpainting to Control the Kinetics and Observation Efficiency of Dynamic Processes in Liquids

Nigel D. Browning[1,2*], B. Layla Mehdi[1,2], Andrew Stevens[2], Libor Kovarik[2], Andrey Liyu[2], Bryan Stanfill[2], Sarah Reehl[2], Lisa Bramer[2]

[1] Mechanical, Materials and Aerospace Eng., University of Liverpool, Liverpool, L69 3GH
[2] Pacific Northwest National Laboratory, Richland, WA 99352, USA
[*] nigel.browning@liverpool.ac.uk

Many processes in materials science, chemistry and biology take place in a liquid environment. Often the final desired outcome of the process is a result of a series of complicated transients (occurring on timescales of milliseconds to nanoseconds), where a change in the order, magnitude or location in each of the steps in the process can lead to a radically different result. Understanding and subsequently controlling the final outcome therefore requires the ability to directly control and observe the kinetics of these transients as they happen. This becomes more of a challenge if we would like to acquire a time sequence of images from the same transient event, perform an in-situ observation, as the effect of the electron beam becomes dominant – the longer the sequence of events the more important the beam. The aim of an in-situ experiment is therefore to efficiently use the dose that is supplied to the sample and to extract the most (spatial and temporal) information from each image. For the STEM, optimizing the dose/data content by the use of sub-sampling and inpainting can increase imaging speed, reduce electron dose by 1-2 orders of magnitude (Figure 1) while at the same time compressing the data stream. Here, the basics of inpainting and results showing its use for in-situ observations of nucleation and growth will be presented. Importantly for all observations, the kinetic control of nucleation/growth using sub-sampling highlights the role of the interfaces in the cell. Sub-sampling and inpainting is not limited to STEM as similar methods can be used in TEM mode to increase the speed of any camera. The potential to apply these STEM/TEM methods together to extract quantitative information from a wide range of in-situ and high resolution observations will also be discussed.

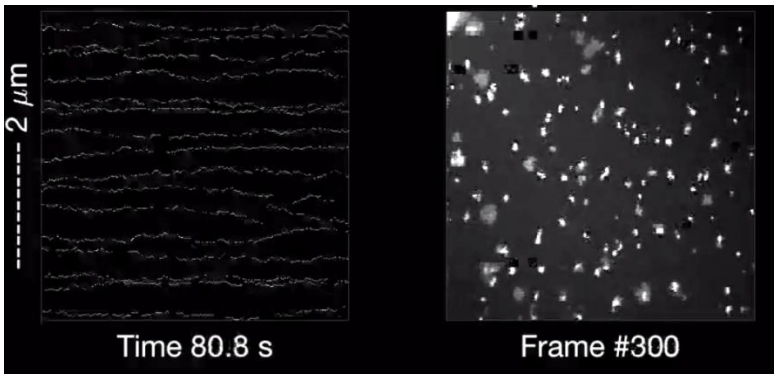

Figure 1: (a) 3% sub-sampled STEM image from an in-situ experiment (b) result of inpainting, showing nucleation and growth of Ag nanoparticles.

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Atomic resolution characterization of GaSb/GaInAs and GaSb/ GaInP wafer bond interfaces for high-efficiency solar cells

Andras Kovács[1], Felix Predan[2], Jens Ohlmann[2], David Lackner[2], Frank Dimroth[2], Rafal E. Dunin-Borkowski[1], Wolfgang Jäger[3*]

[1] Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, Jülich, Germany

[2] Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany

[3] Institute for Materials Science, Christian-Albrechts-University of Kiel, Kiel, Germany

[*] wj@tf.uni-kiel.de

Multi-junction solar cells based on III-V semiconductors reach the highest conversion efficiencies and are currently used primarily in concentrator photovoltaic systems and for power generation on satellites or spacecraft. Several cells of different III-V compound semiconductor materials are generally combined to absorb the solar radiation of different wavelengths and to convert it into electric power. Fabrication of these cells by wafer bonding is of interest since efficiencies of up to 46% have been obtained [1], and efficiencies of up to 50% are within reach. Fast atom beam activation is generally used as a pre-treatment before bonding to remove oxides and contamination [2]. Activation treatment and bond processing often result in the formation of amorphous interface layers with inadvertent impurities [3]. We have applied high-resolution imaging and spectroscopic methods of transmission electron microscopy (TEM) to investigate interface regions in as-bonded and thermally annealed (at temperatures $T \leq 500^{o}C$) GaSb/GaInAs and GaSb/GaInP layer systems. We used aberration-corrected high-resolution TEM, high-angle annular dark-field scanning (S)TEM, and energy-dispersive X-ray spectroscopy (XEDS) with an aberration-corrected probe to monitor elemental distributions with high precision and sub-nanometer spatial resolution.

For GaSb/GaInAs, we find that the crystal lattices are interconnected. The bond interfaces exhibit terraces, misfit dislocations, and nanometer-sized pores, as well as compositional fluctuations in the near-interface regions. For GaSb/GaInP, the interface regions are characterized by an amorphous interlayer about 1.5 nm thick that shows a minor enrichment of Ga. These phenomena are attributed to the wafer pre-treatment before bonding. Thermal annealing, which is often used as a method for improving the electrical interface conductance, results in changes in structure and composition. The amorphous interlayer is reduced in thickness by recrystallization, resulting in a largely epitaxial interface after annealing at 500 ^{o}C. XEDS mapping reveals detectable amounts of In and P after annealing at temperatures $T \geq 225°C$, as well as small pores and In-rich crystalline precipitates for $T \geq 400°C$ in the GaSb near-interface regions. These results provide an understanding of the measured variation of the electrical *I-V* characteristics during annealing [4] and will be compared with results obtained for GaAs/Si wafer-bond interfaces [3]. From a methodological point of view, our results show that the methods of aberration-corrected TEM are instrumental in supporting the development, control, and optimization of concepts for the fabrication of high-efficiency solar cells. An optimized 4-junction solar cell based on GaInP/AlGaAs//GaInAs/Ge currently has an efficiency of 38.5 % at a concentration of 188 suns, while a GaInP/GaAs/GaInAs//GaSb cell has a first efficiency of 29.1 % at 194 suns [1].

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Posters
Abstracts

Scanning distortion correction of STEM images

S. Ning[1], T. Fujita[2], Z. Wang[3], M, Chen[3], and T. Zhang[4*]

[1] Department of Mechanical and Aerospace Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China
[2] WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[3] Department of Materials Science and Engineering, Johns Hopkins University, 3400 N. Charles St. Baltimore, MD
[4] Shanghai University Materials Genome Institute and Shanghai Materials Genome Institute, Shanghai University, 99 Shangda Road, Shanghai 200444, China
[*] zhangty@shu.edu.cn

Various disturbances do exist in the image taking process of scanning transmission electron microscopes (STEM), which seriously reduces the resolution and accuracy of STEM images. In this paper, a deep understanding of the scanning distortion influence on the real and reciprocal spaces of STEM images is achieved via theoretical modeling and simulation. A scanning distortion correction algorithm is further developed based on two images scanned along perpendicular directions, which is able to effectively correct scanning distortion induced deviations and significantly increase the signal to noise ratio of STEM images.

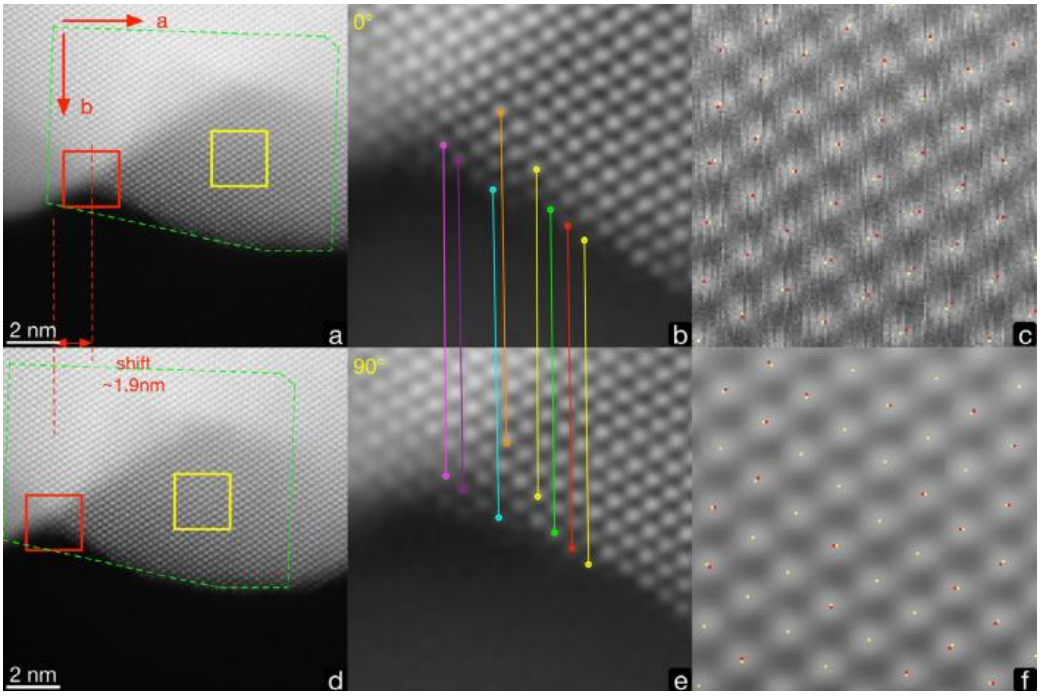

FIG. 1. Scanning distortion correction procedure for STEM images pairs. (a) and (d) are two STEM images of a gold sample obtained by scanning the sample from the horizontal and perpendicular directions. After registering all the atom columns shown in (b) and (e), the influence of the scanning distortion brought by environmental disturbance could be suppressed as shown in (c) and (f).

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Wet-etch Dynamics of High Density 3D Silicon Nanostructures

Z. Aabdin[1,2,3*], U. Anand[1,2], W. W. Tjiu[3], M. Bosman[3], and U. Mirsaidov[1,2]

[1] Centre for BioImaging Sciences and Department of Biological Sciences, National University of Singapore, 117557, Singapore
[2] Department of Physics, National University of Singapore (NUS), 117551, Singapore
[3] Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 3 Research Link, 138634, Singapore
[*] zainul_aabdin@imre.a-star.edu.sg

Wet chemical etching is an important step in fabricating silicon (Si) nanostructures. Existing models propose that wet etching of Si occurs through the reaction of surface Si atoms with etchant molecules, forming etch intermediates that dissolve directly into the bulk etchant solution. In this work, using in-situ TEM [1] we follow the nanoscale wet etch dynamics of Si nanopillars in real-time and show that intermediates generated during alkaline wet etching first aggregate as nanoclusters on the Si surface before diffusing and finally dissolving in the etchant solution. Control experiments with tetramethylammonium hydroxide (TMAH) and isopropyl alcohol (IPA) and molecular dynamics simulation [2] suggests that hydroxyl groups (OH^-) on the Si surface are primarily responsible for holding the nanoclusters of the intermediates at the nanopillar surface. These results suggest that interaction of etch intermediates with etching surfaces is an important parameter in fabricating densely packed 3D nanostructures for future generation microelectronics. With the help of electron energy-loss spectroscopy (EELS), we aim to obtain a deeper understanding of the reaction dynamics by understanding the chemistry of the nanocluster formation during etching.

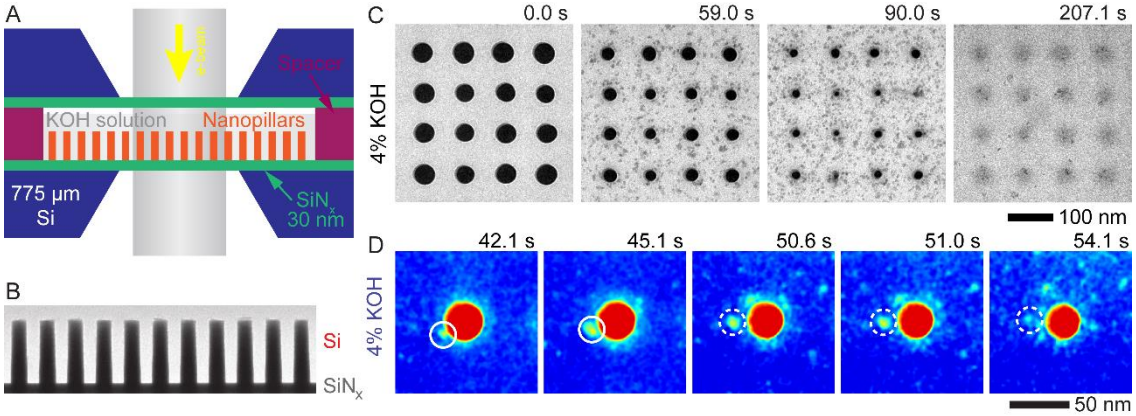

FIG. 1. (A) *Schematic of the in-situ liquid cell platform.* (B) *Side view TEM image of free-standing Si nanopillars on a SiN_x membrane.* (C) and (D) *A series of TEM images showing the etching process of Si nanopillars in 4% aqueous KOH solution and nanoclusters formation.*

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Interlaboratory Comparison for Size and Surface Area of Nanoparticles and Mesoporous Materials

J. Buajarern[1*], V. Yordsri[2], B. Chayasombat[2], A. Klamchuen[3], S. Boonrungsiman[3], S. Prichanont[4], and C. Thanachayanont[2]

[1] National Institute of Metrology, 3/4-5 Klong 5, Klong Luang, Pathumthani, Thailand
[2] National Metal and Materials Technology Center, 114 Thailand Science Park, Klong 1, Klong Luang, Pathumthani, Thailand
[3] National Nanotechnology Center, 111 Thailand Science Park, Klong 1, Klong Luang, Pathumthani, Thailand
[4] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Bangkok, Thailand
[*] jariya@nimt.or.th

Needs for nanosized and nanostructured materials are rapidly growing for various applications, such as industrial catalysis, additives for cosmetics and devices for energy and environment applications. Important factors affecting performances of such nanosized materials are their sizes and surface areas. Determining accurate sizes of nanoparticles is challenging since the commonly used method for size determination, such as transmission electron microscopy (TEM), gives information from only a tiny portion of nanoparticles, and the results could be altered by sample preparations or measurement methods. Moreover, applications of the mesoporous materials are affected by their surface areas, of which the most commonly used method for surface measurement is the BET model on gas adsorption isotherms. This, too, are largely affected by the sample preparations and measurement conditions.

In this study, leading characterization laboratories in Thailand participated in an inter-laboratory comparison of sizes and surface areas of nanoparticles and mesoporous materials. TEM, gas adsorption using BET model and x-ray diffraction (XRD) techniques were used to measure the sizes and the surface areas. Results were compared among different techniques and different laboratories. Sample selection criteria, protocol preparation and results will be presented and discussed.

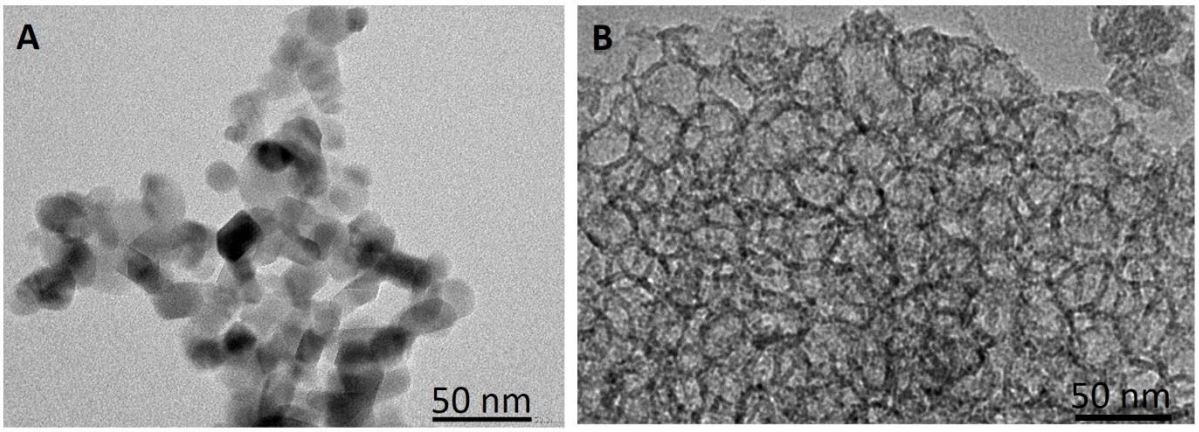

FIG. 1. TEM images of (A) *TiO_2 nanoparticles and* (B) *mesoporous silica material.*

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Fabrication of nanometer accurate high aspect ratio nanopatterns onto liquid cell TEM

Y. Lisunova[1*] and U. Mirsaidov[1]

[1] National University of Singapore, Center for BioImaging Sciences, Physics, 14 Science Drive 4, Singapore 117557
[*] dbsyuli@nus.edu.sg

Liquid cell Transmission Electron Microscopy (TEM) has attracted a lot of research attention owing to its capacity to image at sub-nanometer resolution through liquids. Different materials properties and dynamics have been studied using the Si_3N_4 membranes. Recently, it has been monitored the real-time self-assembly dynamics in nanofluidic channel patterned onto liquid cell membrane [1]. Because of the manufacturing difficulty the nanofluidic channel profile is of high sidewalls surface roughness and exceeds 100 nm which significantly limits its application.

Here, we demonstrate the fabrication of dense high aspect ratio silicon nanopatterns onto the Si_3N_4 membranes with the use of new electron beam lithography (EBL) resist, 'SML' (EM Resist Ltd.) and optimized deep reactive ion etch (DRIE) process parameters. The fabrication process flow is illustrated in Fig1.A. Using SF_6/C_4F_8 etch chemistry [2,3], we found an etch selectivity of SML to Si in the order of 1:4 and etch rate 138 nm/min. Such etch chemistry is extremely useful for direct SML pattern transfer into silicon, without the hard-mask layer, thereby reducing the surface roughness of the substrate material. We achieved dense silicon nanolines of a sub 25 nm half pitch to a depth of 200 nm at 1.2 nm line edge toughness from SEM images (Fig.1.B). This new manufacturing process allows TEM membranes fabrication of target dimension at high accuracy and precision specific to their research. We targeted TEM liquid cells studies on wet chemical etch of the silicon based nanoelectronics and elastocapillary interaction at the nanoscale.

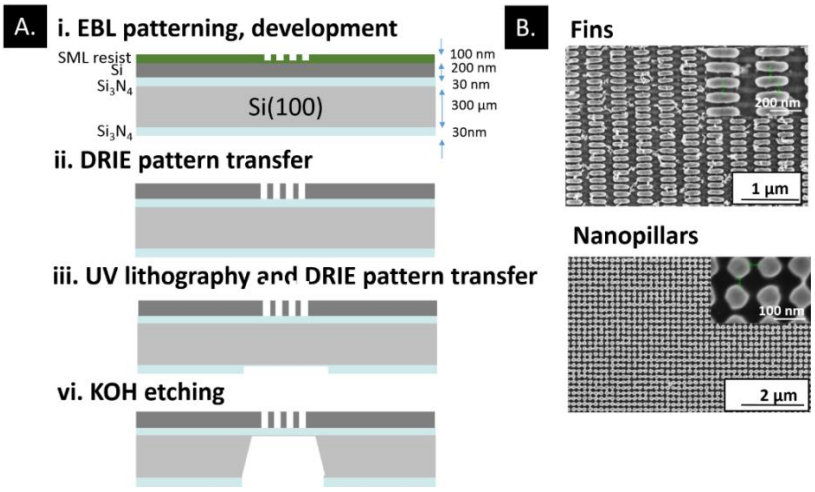

FIG. A. Process flow of the nanometer accurate high aspect ratio silicon nanopatterns fabrication by a combination of EBL patterning and DRIE etch process onto Si/Si_3N_4 membranes. B. SEM images of SML patterns transferred into Si.

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Methylammonium Iodide Effect on the Supersaturation Concentration and Interfacial Energy of the Crystallization of Methylammonium Lead Triiodide Single Crystals

Bichen Li[1], Furkan H. Isikgor[1], Hikmet Coskun[1] and Jianyong Ouyang[1*]

[1] National University of Singapore, Singapore
[*] mseoj@nus.edu.sg

The performance of hybrid organic-inorganic perovskites (HOIP) films greatly depends on their quality. As HOIP films are usually prepared from solution of its precursors, it is very important to study the evolution process from precursors to HOIPs. But the investigation on the growth of perovskite thin films from precursor solution is limited by their polycrystallinity. Study on single crystals can help gain better understanding. In this work, methylammonium lead triiodide ($MAPbI_3$) single crystals grown from precursor solutions with different MAI:PbI_2 ratios were investigated. We observed a V-shaped dependence of the onset temperature of $MAPbI_3$ crystallization on the MAI:PbI_2 ratio. When the MAI:PbI_2 ratio is less than 1.7, the crystallization onset temperature decreases with the increasing MAI:PbI_2 ratio. However, it increases with the increasing MAI:PbI_2 ratio at higher MAI:PbI_2 ratio. These are attributed to the effects of MAI on the supersaturation concentration of precursors and the interfacial energy of the crystal growth. At low MAI:PbI_2 ratio, more MAI can lead to the supersaturation of the precursors at lower temperature. At high MAI:PbI_2 ratio, the crystal growing plans change from (100)-plane-dominated to (001)-plane-dominated. The latter have higher interfacial energy than the former. Hence, the interfacial energy between the crystal growing plans and the precursor solution increases with the increasing MAI solution, leading to higher crystallization onset temperature.

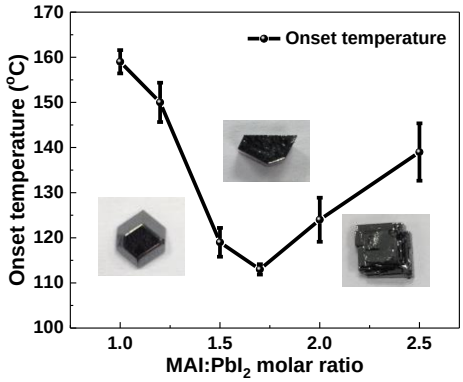

FIG. 1. Variation of the crystallization onset temperature of $MAPbI_3$ with the MAI:PbI_2 molar ratio. The inset photos are single crystals grown from precursor solutions of corresponding MAI:PbI_2 ratios.

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Metal organic frameworks derived Au@Co_3O_4 for electrocatalysis

Wenjie Zang, Cao Guan, Stephen J. Pennycook*, and John Wang

Department of Materials Science and Engineering, National University of Singapore, 117574, Singapore
* steve.pennycook@nus.edu.sg

Metal organic frameworks (MOFs) consisting of abundant reaction sites and porous structure are promising precursors for electrocatalysis. In this paper, uniform two-dimensional Au@ Co_3O_4 nanowalls were fabricated on carbon cloth by a novel two-step facile solution method. The Cobalt-based MOFs were first synthesized via the solution method [1], and then the gold nanoparticles gradually diffused into the MOFs and were embedded by Co_3O_4 during oxidation process. Compared with Co_3O_4 MOF, the Au@Co_3O_4 MOF exhibits better catalytic activity towards oxygen evolution. The enhanced catalytic performance is ascribed to electronegative gold particles, which facilitate the generation of Co^{IV} reaction sites [2].

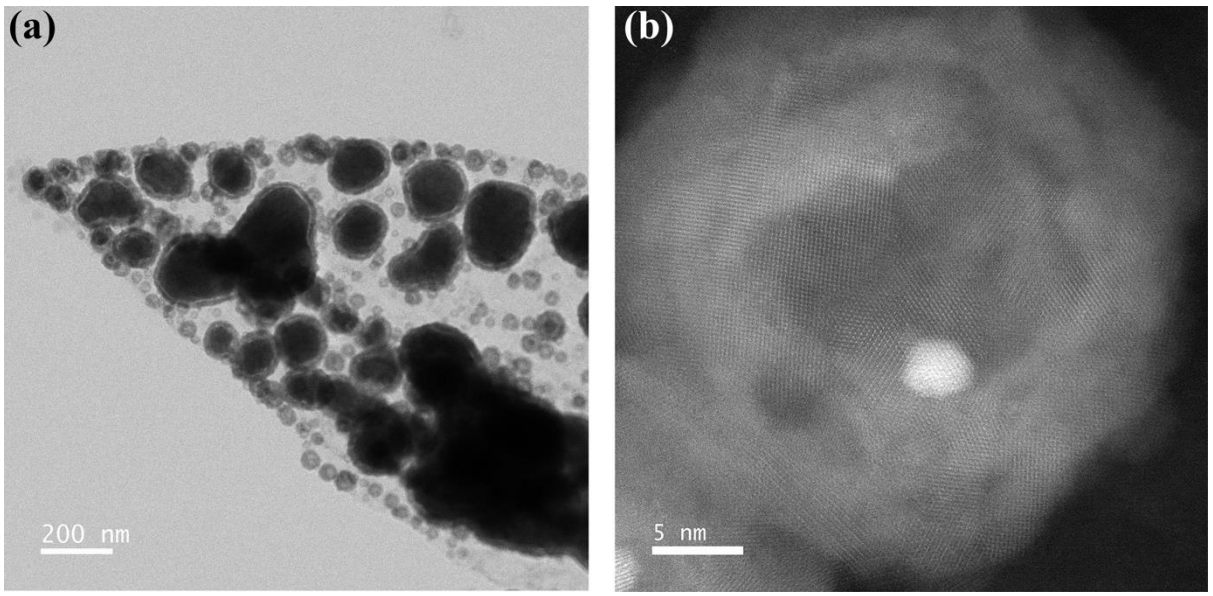

FIG. 1. STEM characterization of the Au@Co_3O_4 nanowall. (A) *Low magnification STEM bright field image showing the morphology of nanowall.* (B) *High magnification STEM HAADF/ABF image showing the structure of Au embedded by Co_3O_4.*

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Structural origin of high piezoelectricity at phase boundary: nanoscale phase coexistence and gradual polarization rotation

Haijun Wu, Jiagang Wu, and Stephen. J. Pennycook*

Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore
* steve.pennycook@nus.edu.sg

Piezoelectric materials interconvert electrical energy into mechanical energy, and are widely used for electronic devices. Almost all are toxic lead-based compounds, which are soon to be banned from use in many regions of the world. Hence, there is an urgent need for replacement by lead-free materials. However, so far, lead-free piezoelectrics have not been able to provide competitive performance to the lead-based materials. Key to the academic problem is a lack of fundamental understanding on the actual mechanisms involved at the microscopic (unit cell) level. While it is understood that giant responses occur near structural phase boundaries, there is at present no atomistic understanding of the origin of the response. New materials have therefore been synthesized largely by informed trial and error.

Recently our team has had notable breakthroughs in improving the properties of (K,Na)NbO_3 (KNN) based [1-2] and $BaTiO_3$ (BT) based [3] perovskite ceramics through alloying to engineer the phase boundaries into the desired temperature regime, and simultaneously improving the temperature stability. Electron microscopy has indicated a hierarchical structure of nanodomains with coexisting phases inside, like in the lead-based compounds. Furthermore, precise mapping of atomic displacements reveals a gradual polarization rotation between coexisting phases, as shown in Fig. 1. By directly observing these atomic-scale structural features, we believe we will achieve new understanding of piezoelectric behavior, and as a result be able to synthesize new lead-free materials, bulk and thin film, to eradicate lead-based products from the marketplace, with concomitant environmental and commercial benefits worldwide.

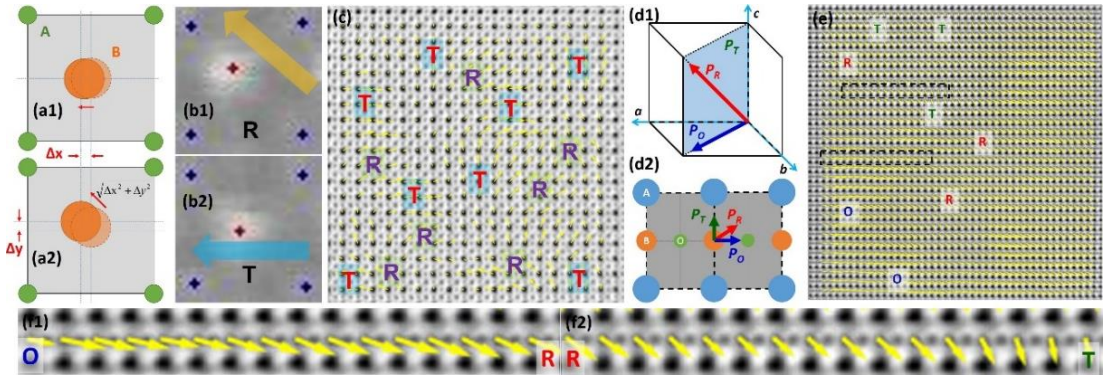

FIG. 1. (a1,a2) and (d1,d2) structural models; (b1,b2) and (c) HAADF and ABF images of KNN-based material with polarization map, R+T; (e) ABF image of BT-based material with polarization map, R+T+O; (f1,f2) Gradual polarization rotation between R, O, and T.

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Atom-by-atom fabrication of freestanding monolayer molybdenum membrane

Xiaoxu Zhao[1], Jiadong Dan[2], Wu Zhou[3], Kian Ping Loh[1*] and Stephen J. Pennycook[2*]

[1] Department of Chemistry, National University of Singapore, Singapore, 117543, Singapore

[2] Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117575, Singapore

[3] School of Physical Sciences, CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, Beijing 100049, China

[*] chmlohkp@nus.edu.sg, & [*] steve.pennycook@nus.edu.sg

Fabrication of materials in the monolayer regime to acquire fascinating physical properties has attracted enormous interest during the past decade, and remarkable successes have been achieved on numerous layered materials adopting weak interlayer van der Waals (vdW) forces [1]. However, fabricating monolayer metal membranes possessing strong intralayer covalent bonds remains elusive. Here, we successfully fabricate freestanding monolayer Mo membranes from monolayer $MoSe_2$ films via selective electron beam (e-beam) sputtering of Se atoms by scanning transmission electron microscopy (STEM) [2]. The growth of the Mo membrane is triggered by the formation and aggregation of Se vacancies as seen by atomic resolution sequential STEM imaging. Various novel structural defects and intriguing self-healing characteristics are unveiled during the growth. Freestanding monolayer metal membranes have never been prepared by conventional growth methods. In addition, the monolayer Mo membrane is highly robust under e-beam irradiation. It is likely that other metal membranes can be fabricated in a similar manner, and these pure metal-based 2D materials would remarkably diversify the category of 2D materials and introduce profound novel physical properties [3].

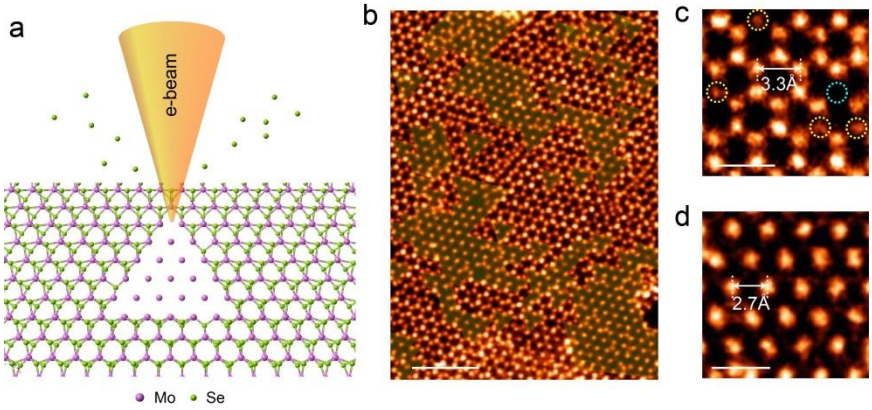

FIG. 1. (a) Schematic illustration of fabrication of freestanding monolayer Mo membrane. (b) STEM-ADF image of as-fabricated freestanding Mo membranes embedded in a monolayer $MoSe_2$ film. (c-d) STEM-ADF images showing the freestanding monolayer $MoSe_2$ film (c) and a monolayer Mo membrane (d). Scale bars: 2nm in (b), 0.5 nm in (c-d).

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STEMPY: A new Python package for microscopy data processing

J. Dan[1], X. Zhao[1], and S.J. Pennycook[2*]

[1] NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, 13 Centre for Life Sciences, #05-01, 28 Medical Drive, Singapore 117456
[2] Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117575, Singapore
[*] steve.pennycook@nus.edu.sg

DigitalMicrograph has long been the industry standard software for (scanning) electron microscopy data processing such as identification [1] and image registration [2]. However, the obscureness of DigitalMicrograph scripting and lack of modern machine learning packages have limited its application in microscopy data processing.

A new package (STEMPY) based on Python has been developed. STEMPY is an independent package that can read and write dm3 or dm4 files from disk. Application examples include atom-by-atom identification based bond order analysis, nanopore mapping (see Fig.1) and edge density calculation in nanoporous MoS_2 films [3], image registration to reveal the growth mechanism of monolayer Mo membranes, and novel filtering techniques to remove the contamination background in atomic resolution STEM images.

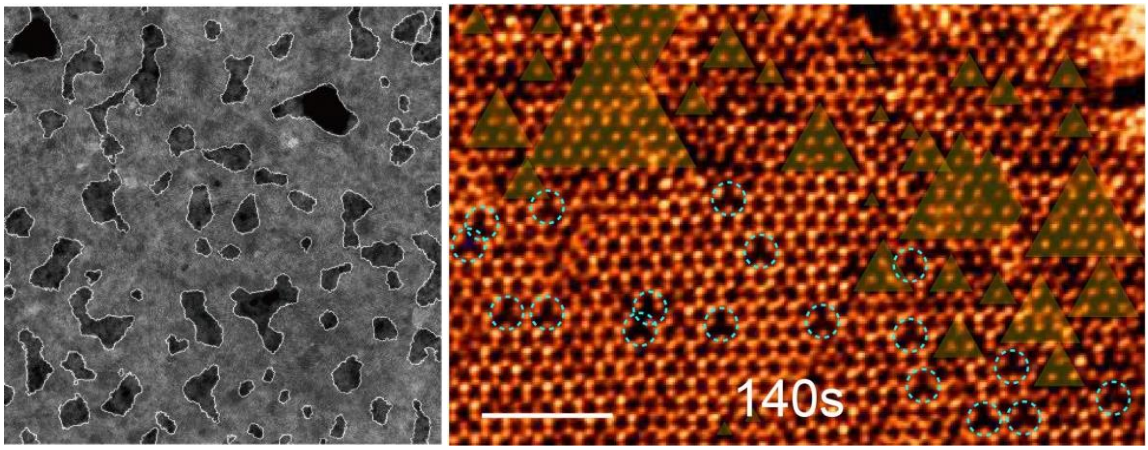

FIG. 1. Left:Nanapore area and edge mapping with their overlaid with raw data. Right: Registered ADF-STEM image of growth of Mo membranes at 140s via e-beam irradiation. Data taken on a JEOL ARM200F with ASCOR corrector at 80 kV.

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Insight into magnetic interaction at nonmagnetic oxide interfaces by atomic-resolution spectrum imaging

M. Li[1], Z. Huang[2], C. Tang[1], C. Li[1, 2], S. J. Pennycook[1*]

[1] National University of Singapore, Department of Materials Science and Engineering, Block EA #07-24, 9 Engineering Drive 1, Singapore 117575
[2] NUSNNI-NanoCore, 5A Engineering Drive 1, Singapore 117411
[*] steve.pennycook@nus.edu.sg

Unusual magnetic interactions that arise at the interface between nonmagnetic oxides have attracted wide interest. This magnetic interaction might be modulated by carrier confinement where the magnetic interaction is mediated by itinerate electrons. Oxide heterostructures $LaAlO_3/SrTiO_3//NdGaO_3$ (LAO/STO//NGO) were designed to demonstrate the effect of carrier confinement on modulating the magnetic interaction on the interface between nonmagnetic oxides (LAO and STO). In such structures, mobile electrons are confined in the STO layer by controlling STO thickness. This heterostructure with thin STO layer (6 unit cells), which has an enhanced carrier confinement, shows much larger magneto-resistance (MR) rather than the one with 10 unit cells of STO. The enhanced MR is believed as the result from strengthened interaction between mobile electrons and localized Ti^{3+} ions due to smaller interaction distance in 6 unit cells STO heterostructures. Atomic-resolution spectrum imaging helped us insight into the magnetic interaction from electronic correlations.

Figure 1A shows STEM-HAADF images of LAO/STO//NGO heterostructures with 6 (left) and 10 (right) unit cells of STO layer, respectively, indicating very clear and smooth interfaces without inter-diffusion. Moreover, atomic-resolution Energy Dispersive X-ray Spectroscopy (EDX) mapping of LAO/STO//NGO (Figure 1B) confirms no La diffusion into TiO_2 terminated STO. The electron energy loss spectroscopy (EELS) was used to confirm the location and amount of Ti^{3+} ions. As shown in Figure 1C, Ti^{3+} ions prefer to locate at the LAO/STO interfaces. Meanwhile LAO/STO//NGO with 6 unit cells of STO has more Ti^{3+} ions, which promotes the stronger interaction between the mobile electrons and Ti^{3+} ions, leading to an observed enhanced magnetoresistance ratio.

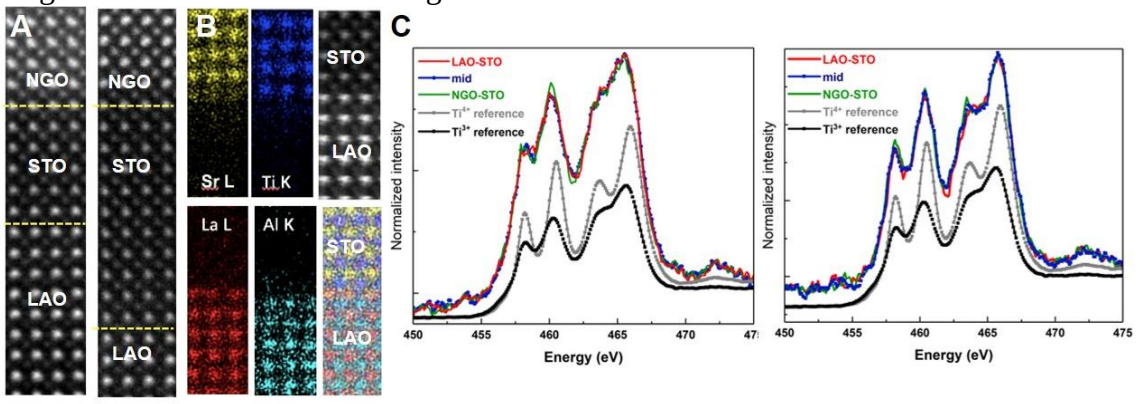

FIG. 1. (A) The STEM-HAADF images of LAO/STO//NGO with 6 and 10 unit cells of STO. (B) Atomic resolution EDX mapping of LAO/STO//NGO with 10 unit cells of STO. (C) EELS spectra of Ti $_{L2,3}$ edge at the LAO/STO interface (red), the middle STO layer (blue) and the STO/NGO interface (green) of LAO/STO//NGO with 6 (left) and 10 (right) unit cells of STO.

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EMCD for in-plane magnetic measurement

Dongsheng Song[1#*], Amir H. Tavabi[2], Zi-An Li[2], András Kovács[2], Ján Rusz[3], Wenting Huang[4,5], Gunther Richter[5], Rafal E. Dunin-Borkowski[2], Jing Zhu[1]

[1] National Center for Electron Microscopy in Beijing, Key Laboratory of Advanced Materials (MOE) and The State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.
[2] Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, D-52425 Jülich, Germany.
[3] Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden.
[4] Institute for Applied Materials, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.
[5] Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, D-70569 Stuttgart, Germany.
[#] Present address: NUSNNI, National University of Singapore, Singapore
[*] nnisong@nus.edu.sg

Electron energy-loss magnetic chiral dichroism is a powerful technique that allows the local magnetic properties of materials to be measured quantitatively with close-to-atomic spatial resolution and element specificity in the transmission electron microscope. Until now, the technique has been restricted to measurements of the magnetic circular dichroism signal in the electron beam direction. However, the intrinsic magnetization directions of thin samples are often oriented in the specimen plane, especially when they are examined in magnetic-field-free conditions in the transmission electron microscope. Here, we introduce an approach that allows in-plane magnetic signals to be measured using electron magnetic chiral dichroism by selecting a specific diffraction geometry. We compare experimental results recorded from a cobalt nanoplate with simulations to demonstrate that an electron magnetic chiral dichroism signal originating from in-plane magnetization can be detected successfully.

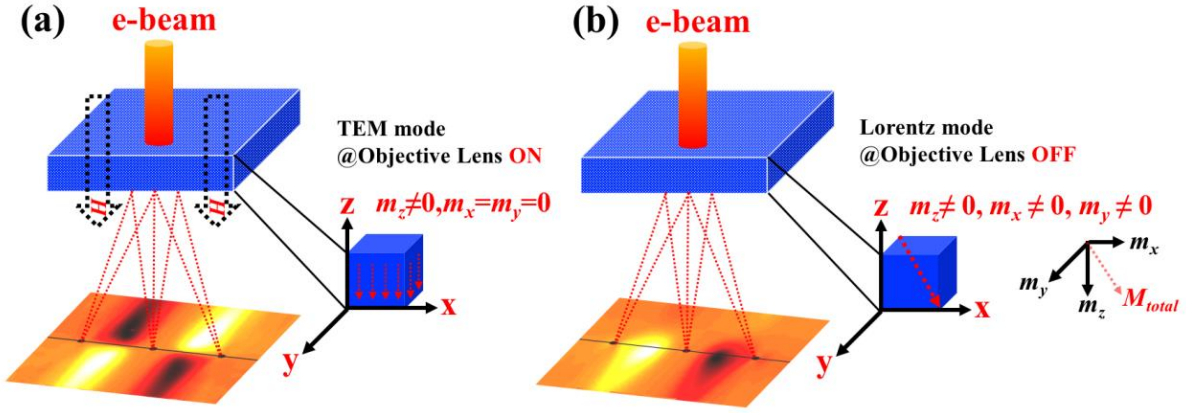

Fig. 1 Schematic diagrams illustrating out-of-plane and in-plane magnetic measurement using the EMCD technique. (a) Diffraction geometry for the EMCD technique in TEM mode with the objective lens on. The magnetization is saturated in the electron beam direction (the z direction) by the strong applied magnetic field, i.e., Mx = My = 0. (b) Diffraction geometry for the EMCD technique in Lorentz mode with the objective lens off.

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Structural origin of high piezoelectricity at phase boundary: nanoscale phase coexistence and gradual polarization rotation

Haijun Wu[1], and Jiagang Wu[2] and Stephen. J. Pennycook[1*]

[1] Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore
[2] Department of Materials Science, Sichuan University, 610064, Chengdu, P. R. China
[*] steve.pennycook@nus.edu.sg

Piezoelectric materials find remarkably wide applications in automotive, electronics, aerospace, medical and consumer products, not only as sensors and actuators, but in humidifiers, microphones, ultrasonic cleaners, printers and many more. Almost all are based on toxic lead-based compounds, which are soon to be banned from use in many regions of the world. Hence, there is an urgent need for replacement by lead-free materials. However, so far, lead-free piezoelectrics have not been able to provide competitive performance to the lead-based materials. Key to the academic problem is a lack of fundamental understanding on the actual mechanisms involved at the microscopic (unit cell) level. While it is understood that giant responses occur near structural phase boundaries, there is at present no atomistic understanding of the origin of the response. New materials have therefore been synthesized largely by informed trial and error.

We propose to replace this situation with a fundamental scientific understanding of the polarization rotation that links mechanical strain to electrical charge. Recently our team has had notable breakthroughs in improving the properties of $(K,Na)NbO_3$ (KNN) based and $BaTiO_3$ (BT) based perovskite ceramics through alloying to engineer the phase boundaries into the desired temperature regime, and simultaneously improving the temperature stability.[1-3]

Electron microscopy has indicated a hierarchical structure of nanodomains with coexisting phases inside, like in the lead-based compounds. Furthermore, precise mapping of atomic displacements reveals a gradual polarization rotation between coexisted phases. With direct observing these atomic-scale structural features, we believe we will achieve new understanding of piezoelectric behavior, and as a result be able to synthesize new lead-free materials, bulk and thin film, to eradicate lead-based products from the marketplace, with concomitant environmental and commercial benefits worldwide.

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Critical thickness for interfacial structural reconstruction at $Sr(Al, Ta)O_3/SrTiO_3$ interface

C. J. Li[1], K. Han[2], C. H. Tang[1], M.S. Li[1] and S. J. Pennycook[1*]

[1] Department of Materials Science and Engineering, National University of Singapore, Singapore 117545
[2] NUSNNI-Nanocore, National University of Singapore, Singapore 117411
[*] steve.pennycook@nus.edu.sg

$Sr(Al, Ta)O_3/SrTiO_3$ interface shows extremely high carrier concentration and low carrier concentration of two dimensional electron gas, evidenced by the quantum magneo resistance with magnetic field B period oscillations, which is normally not observed in oxide interfaces. The unusual properties is found to be linked to interfacial stack faults which is only confined within first 2 uc of the $Sa(Al,Ta)O_3$ near the Sr(Al, Sr) AlO_3 interface. Surprisingly, when the thickness is less than 6 uc, there is only intermixing of Ta with Ti at the interface but a good epitaxial relationship is maintained. When the thickness is 6 uc and above, interfacial stacking faults is accompanied with the Ta/ Ti intermixing. The emergence of the interfacial stacking faults results a reversal of energy level of Ti orbital d_{z2} and d_{x2-y2}, probed by the x—ray linear dichroism, though not accessible by the transport measurement. There are two types of stacking order are observed, shown in Fig. 1a and b, due to the initial cubic symmetry before the structural reconstruction. Supported by the DFT calculation, we report unit cell dependent thickness dependent structural reconstructions at the oxide heterostructures.

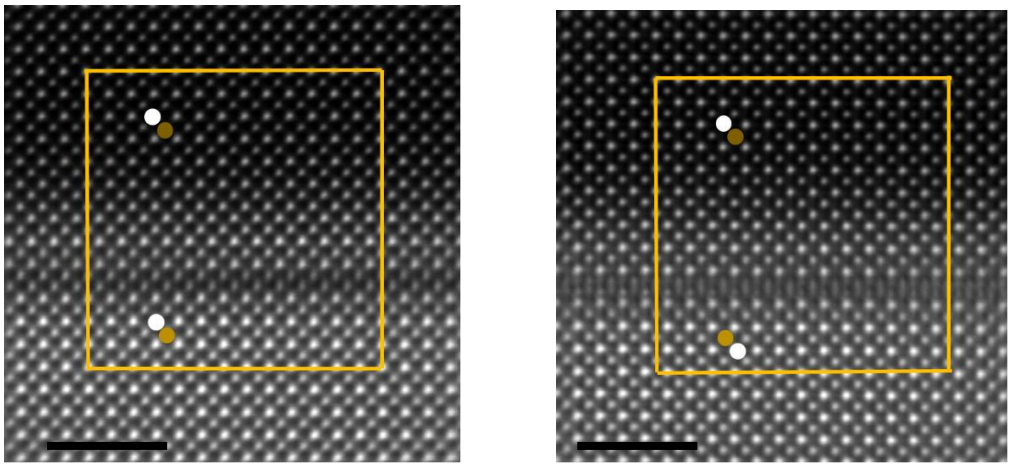

Fig.1 Two types of interfacial structural reconstructions. (a) Interface shows a zig-zag pattern denotes an extra SrO layer between $Sr(Al,Ta)O_3$ and $SrTiO_3$ interface, (b) interface shows streaky pattern across the interface, due to half unit cell shift along the electron beam direction. All images are taken at [100] zone axis, white dot denotes the brighter (heavier) atoms in perovskite structure, while brown atoms shows the darker (lighter) in the perovskites. The yellow box act as guides for the atomic arrangement between $SrTiO_3$ (top) and $Sr(Al, Ta)O_3$ (bottom). The scale bar in the picture is 2 nm.

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[1] This research was supported by the Lee Kuan Yew postdoctoral Fellowship.

Three-dimensional imaging of individual La atom impurities in TiO_2 film with aberration-corrected STEM

C. Tang[1], C. Li[1,2], M. Li[1], S. J. Pennycook[1*]

[1] National University of Singapore, Department of Materials Science and Engineering, Block EA #07-24, 9 Engineering Drive 1, Singapore 117575
[2] NUSNNI-NanoCore, 5A Engineering Drive 1, Singapore 117411
[*] steve.pennycook@nus.edu.sg

Single dopant and impurity atoms sometimes are able to influence materials properties dramatically. Then it becomes more crucial to locate individual atoms. With the recent development of the aberration-corrected scanning transmission electron microscope (STEM), it makes the picometer scale localization of single atoms finally possible. Unfortunately, because generally only a two-dimensional projection can be obtained along a certain direction, some information along this direction is missing. Optical depth sectioning with large-angle illumination STEM is a promising approach to obtain the information from the third dimension, *depth* [1].

STEM with a high-order aberration corrector and cold-FEG allows us to increase the illumination angle to reach nm-scale depth-resolution. It is possible to accurately locate individual atoms along a zone-axis by through-focal series imaging. Figure 1 (A) shows La atoms located at a TiO_2 grain boundary. By a through-focal series of images (Figure 1 (B) and (C)) in <100> zone-axis orientation of TiO_2 the doped La atoms come into focus within a limited focal interval.

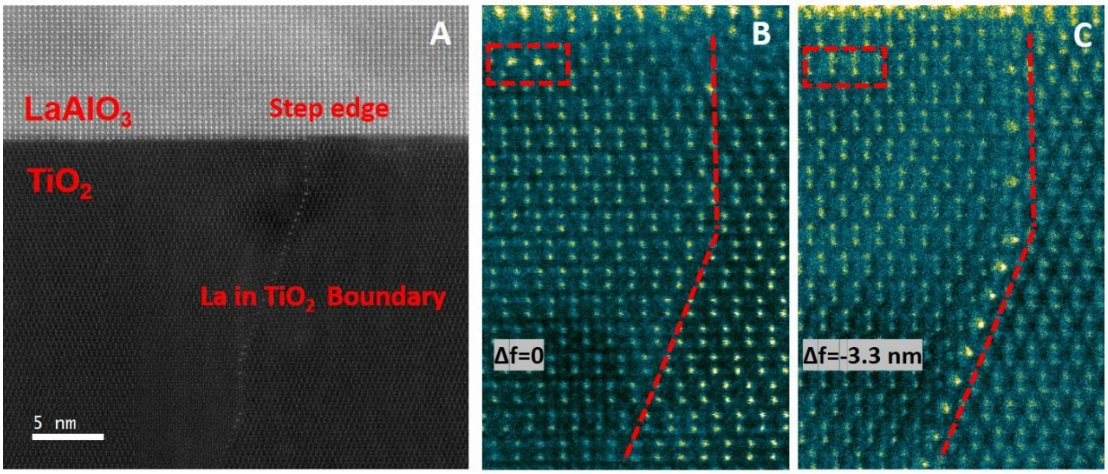

FIG. 1. (A)STEM-HAADF image showing La atoms located at a TiO_2 grain boundary, (B) and (C) are images that are obtained before and after a 3.3 nm through-focal series, respectively. The red rectangle marks two La atoms that go out of focus, and the red dashed line marks a TiO_2 boundary with doped La atoms coming into focus.

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Efficient identification of extrinsic light elements bonded to 2D materials in STEM

Pranjal Kumar Gogoi[1,2*], Andrew T. S. Wee[2], Mark B. H. Breese[1,2], Stephen John Pennycook[3]

[1] Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542
[2] Singapore Synchrotron Light Source, National University of Singapore, 5 Research Link, Singapore 117603, Singapore
[3] Department of Materials Science & Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575
[*] phypkg@nus.edu.sg

Atomic resolution Z-contrast STEM imaging has been immensely successful in revealing the atomic structure of materials in recent times [1]. Particularly, aberration corrected state-of- the-art low voltage STEM has been used extensively for imaging two dimensional materials like graphene and transition metal dichalcogenides, revealing their pristine atomic scale structure including edges, point defects, and grain boundaries [2]. However, detecting extrinsic light elements (like oxygen, nitrogen) bonded to these 2D materials is still a challenge. The main reasons are sample contamination from the transfer process, weak bonding of these extrinsic atoms to the 2D crystal, and very weak contrast due to low HAADF signals. One of the methods employed to detect light elements for transition metal oxide materials has been to use ABF images, which show enhanced contrast for light elements [3].

In this work, with the available facility of simultaneous HAADF, MAADF, ABF, and BF detection in the NUS JEOL JEM-ARM200F STEM, we have performed a systematic study on monolayer WSe_2 and MoS_2. The results reveal some interesting and important features based on the atomic species of the sample and the detector settings. While incoherent Z-contrast imaging is comparatively less sensitive to various factors like local contaminations and possible strain, the phase images show considerable local deviations from the expected results. We perform extensive STEM image simulations for the pristine state and various defect as well as bonding states of the extrinsic atoms based on multislice frozen phonon approximation method.

The most intriguing aspect of these results is the observation of substantially enhanced contrast variations in the MAADF images at single atom sites which otherwise show 'normal' contrast in the HAADF image. Overall, this systematic and combined experimental, simulation, and analytical work enhances our understanding of the fundamental factors affecting the incoherent and coherent STEM images of 2D materials and guides us in implementing an efficient strategy to push the capabilities of STEM imaging to the limit to detect and identify extrinsic light elements in 2D transition metal dichalcogenides.

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Low Dose, High Frame Rate Imaging of Au Nanorod Dynamics in Water

S.W. Chee[1,2,3], U. Anand[1,2,3,4], G. Bisht[2,4] S.F. Tan[1,2] and U. Mirsaidov[1,2,3,4 *]

[1] Department of Physics, National University of Singapore, Singapore 117551
[2] Centre for Bioimaging Sciences and Department of Biological Sciences, National University of Singapore, Singapore 117557
[3] Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore 117546
[4] NUSNNI-NanoCore, National University of Singapore, Singapore 117411
[*] mirsaidov@nus.edu.sg

The ability to visualize dynamics of nanoscale objects is important for understanding the mechanisms behind various biological and chemical processes. While the translation of nanometer-sized particles is relatively straightforward to follow with single-particle tracking techniques based on optical probes, following both translational and rotational motion with such methods is more challenging [1]. Here, we report on our progress in capturing the dynamics of nanoparticles directly with liquid cell transmission electron microscopy (TEM) at high temporal resolution [2]. We will show that the motion of Au nanorods adsorbed on the silicon nitride surface can be captured at 300 frames per second with low electron fluxes of 15-80 $e^-/(Å^2 \cdot s)$. Thickness measurements with electron energy loss spectroscopy indicate that the liquid layers in our liquid cells are around few hundred nanometers thick, which allow us to observe intermittent desorption of nanorods at higher electron fluxes (see Figure 1).

The individual frames acquired under such low dose imaging conditions (which translates no more than 0.4-2 e^-/pixel in a single frame) are very noisy. As such, the spatial resolution of each image will be degraded as described by the Rose criterion [3]. We will briefly discuss the methods that we used to process and analyze such noisy datasets.

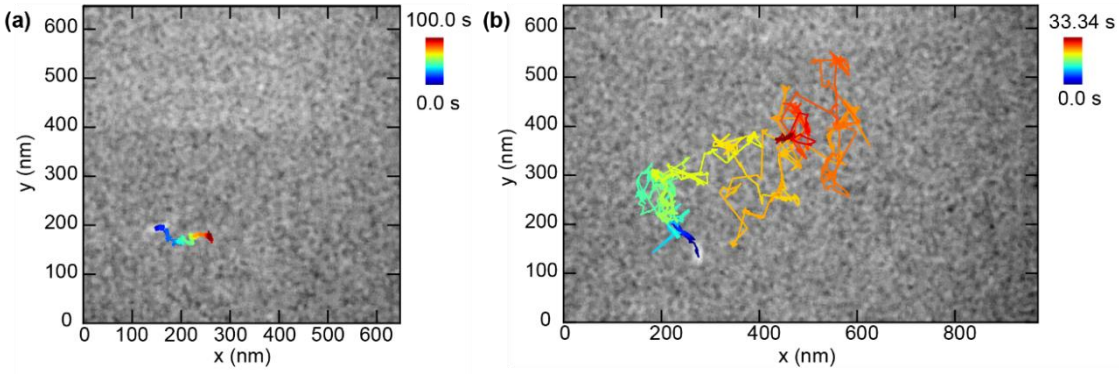

FIG. 1. Comparison of nanorod trajectories tracked at (a) ~16 $e^-/(Å^2 \cdot s)$ and (b) ~44 $e^-/(Å^2 \cdot s)$.

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Visualizing the Self-assembly of Gold Nanoparticles in Solution through *in situ* Microscopy

Shu Fen Tan[1], Geeta Bisht[1] and Utkur M. Mirsaidov[1,2,3,4]

[1] Centre for Bioimaging Sciences and Department of Biological Sciences, National University of Singapore, 14 Science Drive 4, Singapore 117543
[2] Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551
[3] NUSNNI-Nanocore, National University of Singapore, 5A Engineering Drive 1, Singapore 117576
[4] Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117546
[*] phyumm@nus.edu.sg

Hierarchically organized nanoparticles (NPs) are good candidates for plasmonics [1-2] and catalysis [3] studies due to its distinctive properties than its isolated forms. Self-assembly serves as a robust 'bottom-up' method to organize NPs into desired arrays. Here, we use of *in situ* liquid cell electron microscopy to directly probe the self-assembly of chemically-synthesized NPs of different morphologies; Au nanocubes, nanorods, nanospheres and nanobipyramids with surfactant molecules; cetyltrimethylammonium bromide (CTAB) at high temporal and spatial resolution. Our real-time observations reveal that there are different attachment pathways for side-to-side assembly of Au nanocubes. We further investigate how the NP shape and chemical surfactants can affect the NP assemblies to attain the lowest total energy state by monitoring the NP dynamics as a function of time. Understanding the physical and chemical interactions that govern the self-assembly could potentially lay the foundation for rational design of desired assembled nanostructures for applications in catalysis, opto-electronics and drug delivery.

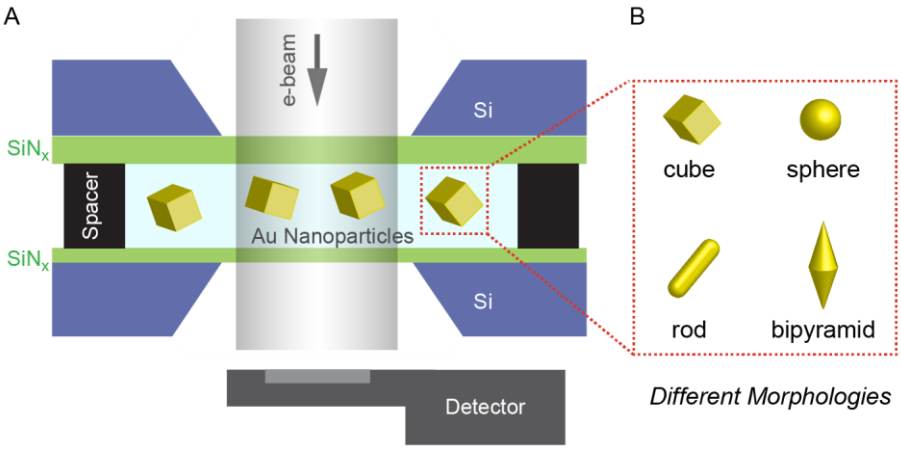

FIG. 1. (A) *Schematic of in situ liquid-cell TEM setup.* (B) *Different morphologies of Au NPs.*

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Visualization of high temperatures 1T-TaS_2 phase transitions in situ in a transmission electron microscope .

P. Machain[1*], E.V. Tyukalova[1], M. Spina[2], S. Garaj[2,3] and M. Duchamp[1]

[1] School of Materials Science and Engineering, Nanyang Technological University, Singapore.
[2] Centre for Advanced 2D Materials, National University of Singapore, Singapore;
[3] Department of Physics, National University of Singapore, Singapore.
[*] paloma001@e.ntu.edu.sg

In this study, we have imaged, in diffraction space, the near-commensurate (NC) charge density waves (CDW) to incommensurate (IC) CDW and metallic phase transition in temperatures ranging from 25 to 70 C in situ a transmission electron microscope (TEM). Despite the limited spatial resolution of the observation in diffraction space, we have characterized, with a spatial resolution better than 20 nm, a free-standing few layers 1T-TaS_2 flakes that were deposited over a trench fabricated on top of MEMs chips (Figs 1.a-c). In the NC phase, the CDW domains are rotated 13.9 degrees with respect to the lattice (Fig. 1d) while, with increasing temperature, they align with the crystallographic lattice in the IC phase (Fig. 1f), as previously observed by XRD [1]. Upon decreasing temperature, the formation of the NCCDW phase appears 5 C below the transition on increasing temperature showing hysteresis. Moreover, the CDW domains are rotated in the negative direction compare to the initial ICCDW configuration before to rotate back to the initial configuration at lower temperature (Fig. 1e). The direction of rotation of the CDW is likely to be strongly affected by the presence of defects, the number of layers as well as the edges configuration. The observation of the NCCDW formation at ~20 nm scale allowed, for the first time, to observe of metastable NCCDW domains near the IC to NC temperature transition.

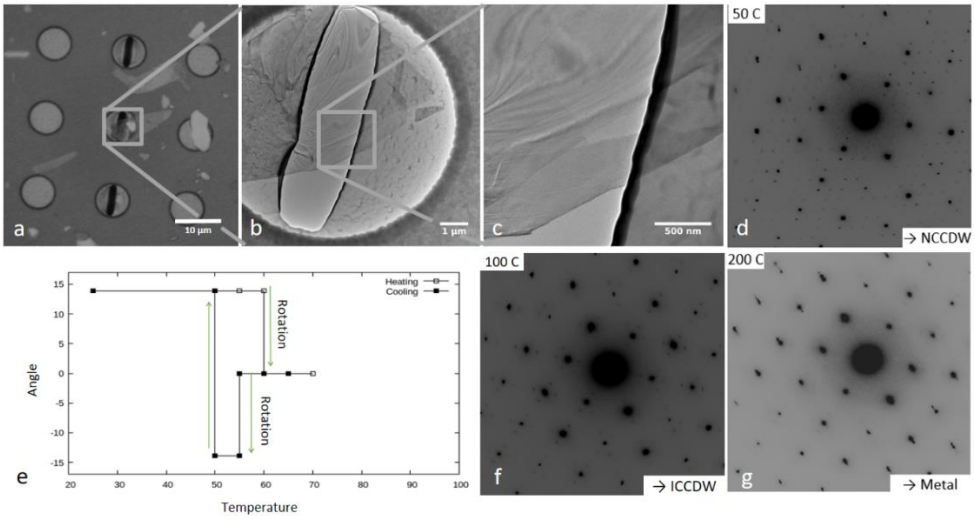

FIG. 1 (a-c) Bright field TEM images at different magnifications of free-standing 1T-TaS_2 flakes. (d, f-g) Selected area electron diffraction pattern (SAED) recorded at the location shown in (c) taken at different temperatures, (d) 50 C, (f) 100 C (g) 200 C upon heating. (e) Angle dependence between the crystallographic and CDW lattices versus temperature.

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Structural evolution of the $LiNi_{0.5}Mn_{1.5}O_4$ cathode material upon *ex situ* cycling by TEM

E.V. Tyukalova[1*], M. Duchamp[1], R. Satish[1], R. C. Yong Sheng[1] and M. Srinivasan[1]

[1] School of Materials Science and Engineering, Nanyang Technological University, Singapore
[*] elizavet001@e.ntu.edu.sg

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a widely used cathode material for Li-ion batteries due to its operating voltage. However, various factors such as oxidation state and atomic coordination of Mn and Ni cation and morphology of the particles influence the performance of LNMO as a cathode material. The purpose of this work is to investigate structural and chemical changes in the LNMO cathode material at the atomic scale when cycling the battery. We first performed, inside a transmission electron microscope (TEM), selected area electron diffraction (SAED) imaging to determine the modification at different cycling states.

The battery cells were assembled in a Swagelok© cell and then were tested on a Arbin BT 2000 at a current rate of 20 mA g^{-1} and cycled between 3.5-5 V vs. Li. Cell 1 and cell 2 were stopped at 5V and 3.5 V respectively and their respective active materials sealed to prevent atmospheric contamination. The pristine phase SAED pattern shows a perfect periodic arrangement of atoms in the structure (Fig. 1a). This is in contrast with the SAED obtained from half and full cycled samples. From the SAED, we deduced that distances between (002) planes vary from 4.0 Å for the pristine phase to 4.1 Å for the half-cycled to 4.2 Å after one full cycle (Fig. 1). Based on this study, we will perform high-resolution scanning (HRSTEM) to track the atomic columns position upon cycling. Moreover, in order to give more quantitative interpretation of the HRSTEM images, experimental and simulated HRSTEM images will be analyzed for different atomic occupancies.

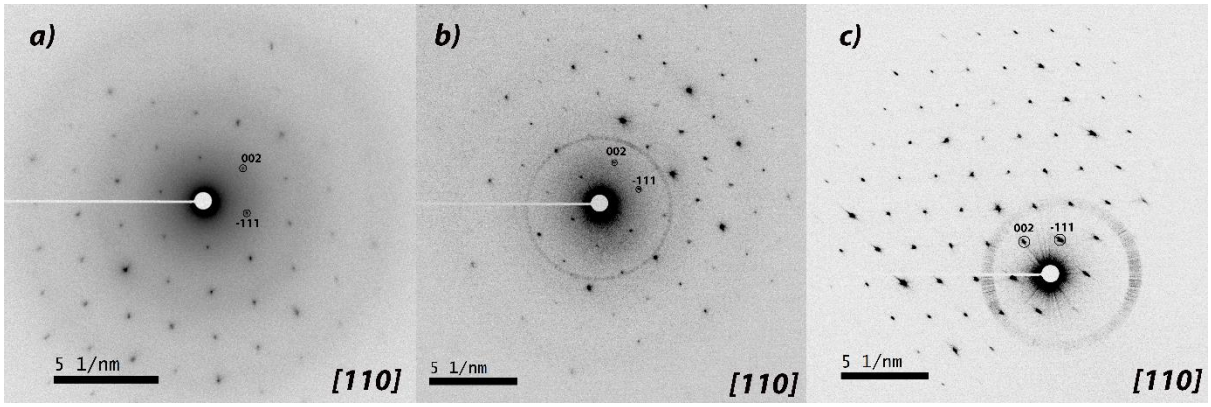

FIG. 1. Selected area electron diffraction pattern along the [110] zone axis from the LNMO cathode (a) pristine sample, (b) after half cycle and (c) after one full cycle. After cycling the changes in atomic distances can be observed.

Interfacial structure of Co_2MnSi/ GaAs (001) heterostructures for spin injection: An atomic resolved EELS study

A. Rath[1,2*], C. Sivakumar[3], S. J. Patel[4], G. Stecklein[5], Paul A. Crowell[5], C. J. Palmstrøm[4], W. H. Butler[3] and P. M. Voyles[1]

[1] Department of Material Science and Engineering, University of Wisconsin-Madison, Madison, WI
[2] Department of Material Science and Engineering, National University of Singapore
[3] Department of Physics & Astronomy, and Center for Materials for Information Technology, University of Alabama, Tuscaloosa, AL
[4] Department of Materials Science and Engineering, University of California-Santa Barbara, Santa Barbara, CA
[5] School of Physics and Astronomy, University of Minnesota, Minneapolis, MN
[*] mseasr@nus.edu.sg

We have studied the interfacial structure and its correlation with the calculated spin polarization in Co_2MnSi/GaAs(001) lateral spin valves. Co_2MnSi (CMS) films were grown on As-terminated c(4x4) GaAs(100) by molecular beam epitaxy using different first atomic layers: MnSi, Co, and Mn. Atomically-resolved Z-contrast scanning transmission electron microscopy (STEM) imaging and electron energy loss spectroscopy (EELS) were used to develop atomic structural models of the CMS/GaAs interfaces that were used as inputs for first principle calculations to understand the magnetic and electronic properties of the interface. First principles structures were relaxed and then validated by comparing experimental and simulated high-resolution STEM images. STEM-EELS results show that all three films have similar six atomic layer thick, Mn and As rich multilayer interfaces. However, the Co-initiated interface contains a Mn_2As-like layer, which is antiferromagnetic, and which is not present in the other two interfaces. Density functional theory calculations show a higher degree of interface spin polarization in the Mn- and MnSi-initiated cases, compared to the Co-initiated case, although none of the interfaces are half metallic. The loss of half-metallicity is attributed to the segregation of Mn at the interface which leads to the formation of interface states.

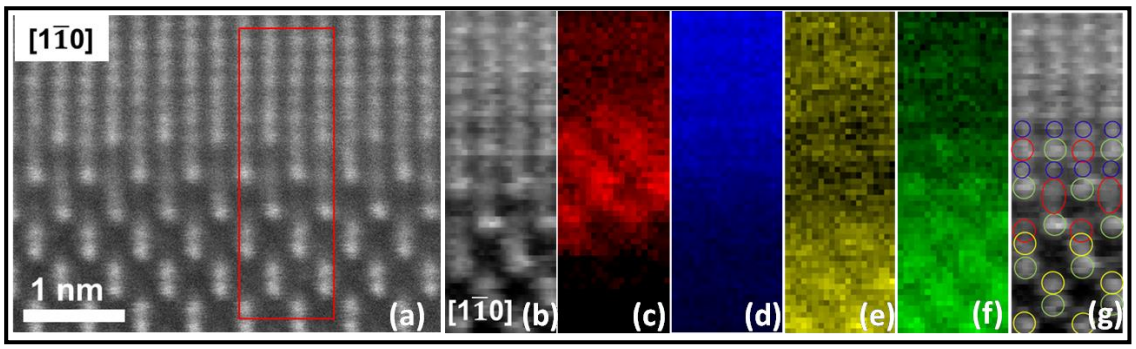

FIG.1: (*a) STEM image of the CMS/GaAs interface (Mn-Si initiated) with location of the EELS maps. (b) ADF image taken in parallel with EELS map. (c-f) Atomic resolution EELS map of Mn (red), Co (blue), Ga(yellow) and As (green). (g) Model image after comparison of EELS map and ADF.*

Real-Time imaging of charged-mediated self-assembly of Au nanocubes and nanospherers using *in situ* liquid cell TEM

C. Li[1,2], S. F. Tan[2] and U. Mirsaidov[2*]

[1] Key Laboratory for Ultrafine Materials of Ministry of Education, and Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China
[2] Centre for Bioimaging Sciences and Department of Biological Sciences, National University of Singapore (NUS), 14 Science Drive 4, Singapore 117543
[3] Department of Physics, NUS, 2 Science Drive 3, Singapore, 117551
[4] NUSNNI-Nanocore, NUS, 5A Engineering Drive 1, Singapore, 117411
[*] mirsaidov@gmail.com

Various self-assembled patterns can be formed on a solid surface through diffusion of colloidal nanoparticles (NPs) dispersed in liquid, for example line, chain, ring and matrix. The assembled structures has attracted strong attention owing to its important applications in sensing[1], catalysis[2], optics[3], and drug delivery[4]. We studied the dynamic of the self-assembly process of positively-charged Au nanocube (GNC) capped with cetrimonium bromide (CTAB) and negatively-charged nanospherers (GNS) capped with citrate in aqueous solution using in situ liquid cell transmission electron microscopy (LC-TEM). The edge length of the GNC and diameter of the GNS are ~30 nm and ~15 nm respectively. Interestingly, we observed the citrate-capped GNS attached sequentially to the CTAB-capped GNC as a result of electrostatic interaction between two oppositely charged ligands. We further characterized the assembly process with UV-Vis spectroscopy and ex situ dry samples TEM imaging to statistically study the most preferable attachment patterns. Our work highlights the role of electrostatic interaction in tuning the nanoparticle assembly which is important for us to understand the formation of complicated nanostructure on solid surface.

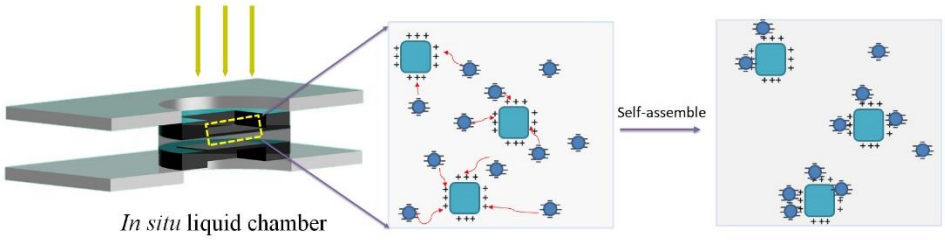

FIG. 1. Schematic diagram of charged-mediated self-assembly process of Au nanocubes and nanospherers

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Understanding the microstructure of cold sprayed metal coatings by advanced electron microscopy

J. Y. Lek[1,2*], A. W. Y. Tan[1,3], A. Bhowmik[1], F. Li[4] and C. B. Boothroyd[2,5]

[1] Rolls-Royce @ NTU Corporate Lab, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
[2] Facility for Analysis, Characterisation, Testing and Simulation (FACTS), Nanyang Technological University, Singapore 639798, Singapore.
[3] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
[4] Rolls-Royce Singapore Pte Ltd, 1 Seletar Aerospace Crescent, Singapore 797565, Singapore.
[5] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
[*] jylek@ntu.edu.sg

Cold spray technology has emerged as a viable option for additive manufacturing and coating of metallic materials. Hence it can be used in repairing damaged engineering parts in various sectors such as marine and aerospace applications. Unlike other thermal spray processes, cold spraying is a solid-state deposition process where the particles bond to the substrate with the aid of a high kinetic energy impact without any melting of the particles. This contributes to the unique microstructure of these coatings.

Several studies of the microstructure of cold sprayed coatings have been reported for different materials systems.[1] The microstructure of Ti-6Al-4V coatings was studied by Birt *et al*., who described the different microstructures present within the coating.[2] In our study, the microstructure of a cold-sprayed Ti-6Al-4V coating has been evaluated specifically at the particle–substrate and particle–particle interfaces to understand the bonding mechanism. Samples were prepared from specific areas of the interfaces by focused ion beam (FIB) milling and then studied with transmission electron microscopy (TEM). Fine grained regions found at the interfaces indicating that the grains are subjected to dynamic recrystallization as a result of severe plastic deformation. The bonding of the particles is attributed to the adiabatic shear instability induced by localized high strain rate deformation and heat accumulation.

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