Electronic Materials and Photonics Division
Room 101A - Session EM+AM+NS+PS-MoA

Atomic Layer Processing: Selective-Area Patterning (Assembly/Deposition/Etching)

Moderators: Michael Filler, Georgia Institute of Technology, Jessica Hilton, RHK Technology

1:20pm **EM+AM+NS+PS-MoA-1 Area-Selective Deposition of Crystalline Perovskites**, *E Lin, **Brennan Coffey**, Z Zhang, P Chen, B Edmondson, J Ekerdt,* University of Texas at Austin

Epitaxial growth of crystalline perovskites enables opportunities in integrating perovskite properties into electronic and photonic devices. Pattern definition is a necessary step in many device applications and definition through etching can be problematic with titanium-based perovskites. We report a process to grow the perovskite film into the final patterned-dimensions through area-selective atomic layer deposition (ALD) followed by epitaxial regrowth from a crystalline substrate to form a single crystal perovskite film. Epitaxial barium titanate (BTO) films can be grown by ALD on strontium titanate (STO(001)) and STO(001)/Si(001) substrates. The substrates are coated with 40 nm of polystyrene (PS) and 185- and 264-nm UV light projected through a shadow mask is used to crosslink the PS under a N_2 atmosphere. The unexposed PS is stripped using toluene to expose the STO surface. Amorphous BTO films are deposited by ALD at 225 °C on the PS-patterned STO(001) surfaces. The low temperature process prevents the degradation of the PS layer. The PS mask is subsequently removed with an oxygen plasma exposure step. Atomic force microscopy and scanning electron microscopy after BTO growth and crosslinked-PS removal demonstrate high fidelity pattern transfer in the BTO films. Reflective high-energy electron diffraction and x-ray diffraction show that the film crystallizes after annealing the sample in vacuum at ≥ 750 °C, with oxygen partial pressure of 1×10^{-6} Torr. Film orientation as a function of annealing temperature is established with transmission electron and piezoresponse force microscopy.

1:40pm **EM+AM+NS+PS-MoA-2 A Dry NF_3/NH_3 Plasma Clean for Removing Si Native Oxide and Leaving a Smooth Si Surface**, ***Christopher Ahles**, J Choi,* University of California, San Diego*; A Kummel,* University of California at San Diego

As devices are scaled to sub 5nm, it is critical to prepare clean and atomically flat surfaces. The traditional aqueous HF clean for removal of native Si oxide suffers from an inevitable air exposure resulting in re-oxidation of the Si surface as well as carbon contamination. The Siconi™ process is a dry clean which utilizes a low temperature (<30C) NF_3/NH_3 based plasma to selectively etch the native oxide layer on Si without etching the underlying Si layer. However the Siconi™ process leaves behind a $(NH_4)_2SiF_6$ salt which must be removed in a subsequent anneal. In this work we present a dry clean which eliminates $(NH_4)_2SiF_6$ salt formation and provides a surface which is just as flat as with the traditional aqueous HF clean.

The silicon surface following removal of the native oxide with an NF_3/NH_3 plasma was studied using X-Ray Photoelectron Spectroscopy (XPS) for elemental analysis as well as Atomic Force Microscopy (AFM) for surface roughness measurements. It was found that when the silicon substrate is held at 65-70C during the etching no $(NH_4)_2SiF_6$ salt formation is observed. The NF_3:NH_3 ratio was found to be a critical parameter for controlling the surface roughness, with the surface roughness decreasing with decreasing NF_3:NH_3 ratios. A NF_3:NH_3 ratio of 1:5 gave a Si surface with an RMS roughness of 3.4nm while a NF_3:NH_3 ratio of 1:10 gave a Si surface with an RMS roughness of 1.9nm. Further decreasing the NF_3:NH_3 ratio is expected to provide an even smoother surface, and experiments towards this end are ongoing. The plasma time was also optimized, and it was found that exposure to the NF_3/NH_3 plasma for 10 seconds and 1 minute resulted in essentially no removal of the native oxide, while exposure for 2 minutes resulted in complete removal of the native oxide. For comparison, Si surfaces cleaned with aqueous HF in our laboratory typically have ~10% oxygen and ~10% carbon contamination, while after cleaning with a NF_3/NH_3 plasma with NF_3:NH_3 = 1:10 for 2 minutes at 70C there was 3% O, 0% C, 4% F and 4% N impurities. Additionally, all of the silicon was in an oxidation state of 0 which means that there was no $(NH_4)_2SiF_6$ salt formation since this salt has silicon in an oxidation state of +4. To validate the applicability of this process, a molybdenum silicide film was deposited via atomic layer deposition (ALD) on dry-cleaned Si as well as on HF cleaned Si. The RMS roughness of the ALD $MoSi_x$ film on the dry-cleaned Si was 2.26nm while on the HF cleaned Si the RMS roughness was 2.78nm. This shows that the dry clean developed in this study is capable of producing cleaner and smoother Si surfaces than the traditional aqueous HF clean.

2:00pm **EM+AM+NS+PS-MoA-3 Probing Strategies for Selective Deposition that Exploit Competitive Interactions**, ***James Engstrom**,* Cornell University **INVITED**

Selective thin film processes, including atomic layer deposition, have the potential to enable next-generation manufacturing and patterning at the 5 nm node and beyond, with direct applications in the nanofabrication of functional layers such as gate dielectrics, metal contacts, and capping/barrier layers. Well-known for its ability to deposit atomically thin films with Å-scale precision along the growth direction and conformally over complex 3D substrates, atomic layer deposition (ALD) has emerged as a key nanomanufacturing process. In this regard, the range and scope of ALD-based applications and capabilities can be substantially extended by also controlling the in-plane growth—a timely and significant development that can be realized *via* area-selective deposition processes that depend on the chemical composition of the underlying surface. In this presentation we will review the approaches that have been taken to achieve area-selective ALD, and we shall highlight both the strengths and shortcomings of these approaches. We will also discuss our efforts to achieve selective deposition that exploit competitive interactions—these interactions can occur both on the surface(s) where the film is, or is not, being deposited, and in the gas phase. In our approach we couple well controlled experiments that involve *in situ* surface analysis using techniques such as X-ray photoelectron spectroscopy and high level quantum chemistry calculations of specific and non-specific binding of molecules to target surfaces. We find that this combination of techniques is capable of shedding considerable light on deposition processes that are both potentially fast and leave no trace of their use in guiding thin film deposition to those areas where growth is desired.

2:40pm **EM+AM+NS+PS-MoA-5 The Interconnect Resistivity Bottleneck**, ***Daniel Gall**, T Zhou, E Milosevic,* Rensselaer Polytechnic Institute*; P Zheng,* Micron Technology

The effective resistivity of conventional Cu interconnect lines increases by more than two orders of magnitude as their width is decreased from 30 to 6 nm. The resulting increase in signal delay and energy consumption limits downscaling of integrated circuits. This presentation will discuss the search for the most conductive metal solutions for narrow interconnect lines, focusing on three key aspects. (i) Electron surface scattering: In situ transport measurements on epitaxial Cu(001) layers with various monolayer cap-layers demonstrate specular electron surface scattering when the local surface density of states at the Fermi level is negligible, resulting in a considerable copper resistivity reduction. (ii) Alternative metals: The resistivity scaling at reduced dimensions is measured using epitaxial metal layers (Cu, Ag, W, Ta, Ru, Mo, Ni) and directly compared to results from classical transport models using first-principles electronic structure calculations. Multiple elemental metals are expected to be more conductive than Cu for polycrystalline lines <10 nm. (iii) Confined transport model: First-principles non-equilibrium transport simulations in combination with measurements of the resistivity vs roughness and dimensionality are used to develop a new model that accurately accounts for electron surface scattering in quantum-confined 1-D and 2-D conductors. This model will replace semiclassical models that fail to predict the resistivity <10 nm.

3:00pm **EM+AM+NS+PS-MoA-6 Sub 0.3 micrometer Copper Patterns Etched with a Plasma-Based Process and Pattern Dependent Electromigration Failure Mechanism**, ***Yue Kuo**,* Texas A&M University

Copper (Cu) is a popular interconnect material for high density ICs, large area TFT LCDs, and many advanced electronic and optical devices. Since Cu does not form volatile products under the conventional plasma etching condition, the only available method in preparing fine lines is the chemical mechanical polishing (CMP), i.e., the single or dual damascene, method. The author's group has invented a new plasm-based Cu etching method that has a high rate at room temperature (1). This method has been successfully demonstrated in defining submicron lines for IC chips as well as being used in the large area TFT LCDs (2). However, this are few papers on defining the sub 0.5 micrometer Cu line using this new etch method. The lifetime of the plasma-etch Cu line on the flat and stepped surfaces has been studied with the electromigration method (3,4). However, the pattern size effect is rarely discussed.

In this talk, the author will discuss the process that can be used to prepare sub 0.3 micron dimension Cu patterns. The success of this process is due to the simultaneous Cu conversion reaction and sidewall passivation. In addition, the failure mechanism of the plasma-etched Cu line over a large range of line widths, i.e., from 1.5 to 30 micrometers, will be examined based on the electromigration test result. In summary, Cu lines prepared from the plasma-based process can be reliably applied in the many nano electronic and photonic products.

1. Y. Kuo and S. Lee, *Jpn. J. Appl. Phys.***39**(3AB), L188-L190 (2000).

2. Y. Kuo, *Proc. 16th Intl. Workshop on Active-Matrix Flat Panel Displays and Devices*, 211-214 (2009).

3. G. Liu and Y. Kuo, J. Electrochem. Soc., 156(6) H579-H584 (2009).

4. C.-C. Lin and Y. Kuo, *J. Vac. Sci. Technol. B*, 30(2), 021204-1 (2012).

3:40pm **EM+AM+NS+PS-MoA-8 The Effect of Metal Diffusion on Contacts to Semiconducting Chalcogenides: Examples for 2D and 3D Materials***,* ***Suzanne E. Mohney****, K Cooley, M Abraham, A Domask, H Simchi, L Kerstetter, C Lawrence, T Walter,* The Pennsylvania State University**INVITED**

We review our recent studies of contacts to a variety of chalcogenide semiconductors, including few-layered molybdenum disulfide and tungsten diselenide, as well as the phase-change material germanium telluride. In some cases, diffusion of a transition metal into the semiconductor has been correlated with an especially low contact resistance. For example, annealing silver contacts on field effect transistors fabricated from few-layered molybdenum disulfide resulted in a reduction in contact resistance by a factor of 4–5 to 0.2–0.7 kOhm-µm, while the ON/OFF current of the device remained high. Diffusion of silver into molybdenum disulfide was confirmed by secondary ion mass spectrometry. On the other hand, nickel appears to be even more soluble in molybdenum disulfide (as observed by Auger electron spectroscopy), but annealing nickel contacts resulted in an increase in resistance. For the phase-change material germanium telluride, incorporation of iron seems to play a role in achieving a low contact resistance of 0.004 Ohm-mm in annealed Au/Fe/Sn/*p*-GeTe contacts. Diffusion of iron into germanium telluride at a low but detectable level was found beneath a narrow-gap tin telluride interfacial reaction product using energy dispersive spectroscopy in the scanning transmission electron microscope. Using only iron or tin without the other did not result in such a low contact resistance. The influence of iron on the electronic properties of germanium telluride is now under study. Besides diffusion of metals into the semiconductor, we also present cases of reactive contacts to germanium telluride, whereby the contact resistance is greatly increased by interfacial reactions that led to the formation of a new phase (especially nickel tellurides and platinum tellurides). Finally, we consider the influence of surface diffusion on quasi van der Waals epitaxy of metals on layered transition metal dichalcogenides.

4:20pm **EM+AM+NS+PS-MoA-10 TiN_x and TaN_x Films via Low-T Thermal ALD using Anhydrous N_2H_4***,* ***Steven Wolf****, M Breeden, M Kavrik,* University of California at San Diego*; D Alvarez, J Spiegelman,* RASIRC*; M Naik,* Applied Materials*; A Kummel,* University of California at San Diego

For device back end of line processing, there is a need to deposit conformal barrier layers on high aspect ratio 3D architectures via low-T ALD. Titanium nitride (TiN) and tantalum nitride (TaN) have been studied as diffusion barriers to WF_6 during W metal fill and to Cu, as Cu can readily diffuse, causing device reliability issues. Organometallic-grown films are required when Cu is present to prevent etching, however, metal halide precursors are preferred for gate stack applications as films typically contain lower levels of carbon and oxygen contamination; this has been correlated with improved film conductivity. This work aims to deposit thermal ALD titanium nitride and tantalum nitride utilizing anhydrous N_2H_4 at lower temperatures than previously reported with NH_3 while still maintaining good film properties.

In this study, low temperature thermal ALD TiN_x from anhydrous N_2H_4 vs. NH_3 and $TiCl_4$ was performed on degreased and UHV annealed SiO_2/Si substrates at temperatures of 300°C and 400°C. The deposited films were studied using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). TaN_x films were grown at 150°C utilizing N_2H_4 and tris(diethylamido) (*tert*butylimido)tantalum (TBTDET) and characterized similarly. In addition, the resistance of air-exposed ultra-thin films was measured using a 4-point probe technique. Resistivities were estimated from thicknesses obtained from cross-sectional scanning electron microscopy (SEM) images. First, saturation dosing was performed to determine optimal half-cycle pulses of $TiCl_4$ and N_2H_4. After TiN_x ALD cycles, AFM imaging showed uniform deposition with sub-nanometer RMS surface roughness. The corrected and normalized XPS showed near stoichiometric Ti_3N_4 with low O and C and ~10% Cl. There was approximately 2x more O and C and 50% more Cl in NH_3 grown films at 400ºC. N_2H_4 films exhibited lower resistivities (359 vs. 555 µohm-cm), attributed to this lower contamination and likely better nucleation density. For TaN_x films, XPS of 15 cycles ALD TaN_x films resulted in 9% O and 4% C and had a Ta/N ratio of 4/5. Analysis on the Ta 4d peaks confirmed nucleation after the initial exposure of TBTDET (Si-O-Ta formation) based on the Ta 4d 5/2 peak BE of ~231.5 eV. A chemical shift to 229 eV was observed upon forming Ta-N bonds. Resistance measurements indicated insulating films consistent with the formation of Ta_3N_5. In summary, N_2H_4 grown TiN_x films showed lower resistivities with fewer impurities. The anhydrous N_2H_4 chemistry was extended to an organometallic Ta precursor, in which nearly stoichiometric films were deposited with low contamination at a modest substrate temperature of 150ºC.

Materials and Processes for Quantum Computing Focus Topic

Room 203A - Session MP+AM+EM+NS-MoA

Systems and Devices for Quantum Computing II

Moderator: Josh Mutus, Google Inc

1:20pm **MP+AM+EM+NS-MoA-1 Quantum Engineering of Superconducting Qubits***,* ***William Oliver,*** MIT Lincoln Laboratory **INVITED**

Superconducting qubits are coherent artificial atoms assembled from electrical circuit elements and microwave optical components. Their lithographic scalability, compatibility with microwave control, and operability at nanosecond time scales all converge to make the superconducting qubit a highly attractive candidate for the constituent logical elements of a quantum information processor. Over the past decade, spectacular improvement in the manufacturing and control of these devices has moved superconducting qubits from the realm of scientific curiosity to the threshold of technical reality. In this talk, we review this progress and our own work at MIT that are creating a future of engineered quantum systems.

2:00pm **MP+AM+EM+NS-MoA-3 The Quantum Socket: A Wiring Method for Superconducting Quantum Computing***,* ***Matteo Mariantoni,*** University of Waterloo, Canada **INVITED**

I will provide a brief introduction to the main technological and scientific challenges to be faced in order to build a practical quantum computer, with emphasis on the case of superconducting quantum computing. I will then delve into a detailed explanation of a method to address the wiring of a two-dimensional array of superconducting quantum bit (qubits): The quantum socket [1]. Next, I will show how the quantum socket can be extended to a medium-scale quantum computer and how it can help mitigate coherent leakage errors due to qubits interacting with spurious cavity modes [2]. I will then show thermocompression bonding technology [3], a method that allows us to further protect qubits from the environment. In particular, I will propose a new qubit design based on our experimental implementation of thermocompression bonded chips, where vacuum gap capacitors are used to reduce dissipation due to so-called two-level state defects in amorphous dielectrics, which are the insulators presently use in our qubits.

[1] J.H. Béjanin, T.G. McConkey, J.R. Rinehart, J.D. Bateman, C.T. Earnest, C.H. McRae, Y. Rohanizadegan, *D. Shiri*, B. Penava, P. Breul, S. Royak, M. Zapatka, A.G. Fowler, and **M. Mariantoni**, Three-Dimensional Wiring for Extensible Quantum Computing: The Quantum Socket, Phys. Rev. Applied **6**, 044010 (2016)

[2] T.G. McConkey, J.H. Béjanin, C.T. Earnest, C.R.H. McRae, Z. Pagel, J.R. Rinehart, **M. Mariantoni**, Mitigating Coherent Leakage of Superconducting Qubits in a Large-Scale Quantum Socket, Quantum Sci. Technol. 10.1088/2058-9565/aabd41 (2018)

[3] C.R.H. McRae, J. H. Béjanin, Z. Pagel, A.O. Abdallah, T.G. McConkey, C.T. Earnest, J.R. Rinehart, and **M. Mariantoni**, Thermocompression Bonding Technology for Multilayer Superconducting Quantum Circuits, Appl. Phys. Lett. **111**, 123501 (2017)

2:40pm **MP+AM+EM+NS-MoA-5 Pogo Pin Packaging for High Coherence Qubits***, **Nicholas Bronn**, V Adiga, S Olivadese, O Jinka,* IBM, T.J. Watson Research Center*; X Wu,* National Institute of Standards and Technology*; J Chow,* IBM, T.J. Watson Research Center*; D Pappas,* National Institute of Standards and Technology

The connectivity between qubits in large superconducting quantum processors prevents the qubits from being addressed by control lines routed to the edge of the chip. In these nontrivial circuit topologies, internal qubits must instead be coupled to control and measurement electronics by a nonplanar technique. Here we present a pogo package consisting of commercially available parts and requiring modest machining tolerances. Through careful engineering of the package for cryogenic and microwave considerations, we measure high coherence times and gate fidelities for qubits in a quantum processor connected by pogo pins. This work was supported by IARPA under contract W911NF-16-1-0114-FE.

3:00pm **MP+AM+EM+NS-MoA-6 50 Ohm Superconducting Kinetic Inductance Traveling-Wave Amplifier with flexible pump frequency for Four Wave Mixing and Three Wave Mixing***, **Xian Wu**, M Bal, J Long, H Ku, R Lake, D Pappas,* National Institute of Standards and Technology

We developed a 50 Ohm transmission-line based superconducting kinetic inductance traveling-wave (KIT) amplifier using high inductance material NbTiN. The nonlinearity originates from the kinetic inductance of the superconductor and enables amplification. Often, the impedance of the transmission line is significantly higher than the 50 Ohm microwave environment due to the dominance of kinetic inductance over geometric inductance at micron size scales. To address this impedance mismatch, we engineered “fingers” on each side of the original coplanar waveguide KIT [1] to introduce extra capacitance that decreases the impedance to approximately 50 Ohm [2,3]. Those extra “fingers” also function to create a band stop at higher frequency to bend the dispersion relation between wave vector (k) and frequency (f), which allows us to apply the pump frequency within a wide span of a few GHz and achieve several GHz gain bandwidth for chosen pump frequency. Another advantage of this structure is that it significantly reduces the phase velocity, hence shortening the physical length of this device. Gain measurements based on both four wave mixing and three wave mixing will be presented.

[1] Appl. Phys. Lett. **108**, 012601 (2016); https://doi.org/10.1063/1.4937922

[2] Journal of Applied Physics **119**, 083901 (2016); https://doi.org/10.1063/1.4942362

[3] Appl. Phys. Lett. **110**, 152601 (2017); https://doi.org/10.1063/1.4980102

3:40pm **MP+AM+EM+NS-MoA-8 Near Term Development of Short Depth Quantum Processors***, **Jerry Chow**,* IBM Research Division, T.J. Watson Research Center **INVITED**

Quantum processors are currently in their infancy though the community is poised to explore bringing them to a state where they can outperform classical computations in relevant application. The challenges that lie ahead are plentiful and touch all aspects of the quantum computer, ranging from finding algorithms to building control software and control hardware as well as engineering and fabricating and testing the quantum hardware. In an effort to accelerate the development of quantum computing IBM launched the IBM Q experience. The Q Experience is a cloud-based platform which allows anyone to get familiar with quantum computing. It allows users to run experiments on actual quantum hardware.

In this talk I will focus on the development and characterization of short depth superconducting quantum hardware. Crosstalk and decoherence are some of the most pressing issues that we face today. Decoherence limits the number of operations that can be performed on the hardware (the depth of the circuit) whereas crosstalk can limit what operations can be performed in parallel on the circuit. The processors featured on the IBM Q experience are based on fixed frequency transmon qubits with a cross-resonance based two qubit gate. For this platform only a very narrow frequency range for the qubits is possible. This leads to problems related to frequency crowding and spurious interactions. Methods for characterizing and addressing both the frequency allocation and characterizing crosstalk will be discussed.

4:20pm **MP+AM+EM+NS-MoA-10 Frequency Crowding in Lattices of Transmon Qubits***, **Sami Rosenblatt**, J Hertzberg, J Chavez-Garcia, N Bronn, H Paik, M Sandberg, E Magesan, J Smolin, J Yau, V Adiga, M Brink, J Chow,* IBM, T.J. Watson Research Center

A key goal in quantum computing is to develop scalable fault-tolerant quantum logic circuits. One promising architecture involves lattices of fixed-frequency transmon qubits coupled via cross-resonance gates. Fixed-frequency qubits offer high coherence and the all-microwave gate reduces circuit complexity. To optimize gate performance, excitation energies of neighboring qubits must be similar but non-degenerate. This architecture is thus sensitive to any variation in device parameters affecting transmon frequency. In this talk we will discuss a statistical model for the resulting ‘frequency crowding’ behavior, and suggest improvements in both architecture design and qubit fabrication in order to achieve scalable circuits with good gate fidelity.

*We acknowledge support from IARPA under Contract No. W911NF-16-0114.

Thin Films Division
Room 104B - Session TF+AM+EM+PS-TuM

Atomic Layer Processing: Area Selective Deposition

Moderators: Christophe Vallee, LTM - MINATEC - CEA/LETI, France, Steven George, University of Colorado at Boulder

8:00am **TF+AM+EM+PS-TuM-1 New Approaches for Area-Selective Atomic Layer Deposition: Inspiration from Etching***, **Adrie Mackus**,* Eindhoven University of Technology, The Netherlands, Nederland **INVITED**

While selectivity has always been one of the most important features of an etching process, only in recent years there has been significant interest in selectivity for deposition, motivated by the application of area-selective deposition in self-aligned fabrication. With selective etching being a more mature technology, previous work in etching can serve as inspiration for how to make deposition processes selective. For example, inhibition layers have been employed in etching to obtain selectivity. Similarly, the use of small molecule inhibitors is currently being explored for achieving area-selective atomic layer deposition (ALD).[1]

Moreover, with the recent advancements in atomic layer etching (ALE), new opportunities emerge for selective processing of material based on novel combinations of ALD and ALE. In recent work, ALE cycles have been implemented in area-selective ALD processes to improve the selectivity.[2]

In this presentation, the similarities between etching and area-selective ALD will be described, in order to discuss what the area-selective ALD community can learn from previous work in etching. Recent developments in area-selective ALD will be illustrated by discussing new area-selective ALD approaches based on the use of inhibitors in ABC-type (i.e. three-step) ALD cycles, and on supercycles combining ALD and ALE cycles.

1. A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, and A.J.M. Mackus, *ACS Nano* **11**, 9303 (2017)

2. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A.***35**, O1B104 (2017)

8:40am **TF+AM+EM+PS-TuM-3 Nucleation of HfO_2 on Si, SiO_2 and TiN Substrates in PE-ALD Processes Investigated by In situ Ellipsometry and Optical Emission Specroscopy (OES)***, **Marceline Bonvalot**, S belahcen, V Pesce, A Chaker, P Gonon, C Vallée, A Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

It is generally admitted that the physical properties of ultrathin layers elaborated by ALD processes are strongly dependent upon the very initial stages of layer growth, defined as the nucleation step. This nucleation step may for instance affect the cristallinity and the texturation of the material when growing in a crystalline state, it can also significantly contribute to the sharpness of the interface between the substrate and the growing material and/or determine the layer density and surface rugosity. Moreover, this nucleation step also plays a major role in the advancement of Selective Area Deposition Processes (SALD), which are considered, as of today, as a very promising approach for the development of bottom-up routes alternative to increasingly expenseive thin layer patterning processes. In these regards, a good knowledge of the phenomena affecting the nucleation mechanisms in ALD is required.

In this work, the initial stages of layer growth has been investigated during the deposition of HfO_2 by Plasma-Enhanced ALD in a FlexAL set-up equipped with an ALE (Atomic Layer Etching) bias system developed by Oxford. Four types of substrates have been put on trial for this purpose, namely, HF last treated Si(100), SiO_2 (45 nm dry oxide)/Si, SiO_2 (500 nm wet oxide)/Si, and TiN (15 nm ALD)/Si. Several in situ surface treatments have been applied on these substrates, prior to HfO_2 ALD cycles with TEMAH as hafnium precursor. They include exposure to a plasma treatment composed of either Ar, CF_4 and O_2 or any mixture of these gases. A very low power (1-10 W) can be applied on the substrate to allow low DC self-bias voltage, which determines energies of ions extracted from the plasma in the vicinity of the substrate. This bias in turn allows an estimation of the contribution of both chemical and physical plasma-surface interactions to the growth mechanism. The nucleation process is followed in situ by spectroscopic ellipsometry assisted by Optical Emission Spectroscopy for the identification of plasma active species and desorbed by-products.

This presentation will describe how the nucleation time on different substrates can be successfully tuned, either delayed or accelerated, thanks to appropriate in situ surface treatment parameters, without inducing any significant perturbation in the subsequent steady state layer growth. These results will be discussed in view of literature data and potential applications to the development of selective ALD.

9:00am **TF+AM+EM+PS-TuM-4 Topographical Selectivity with BN Electron-Enhanced ALD***, **Jaclyn Sprenger**, A Cavanagh, H Sun,* University of Colorado at Boulder*; A Roshko, P Blanchard,* National Institute of Standards and Technology*; S George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is a new growth technique using sequential self-limiting exposures of electrons and precursor. The electrons produce dangling bonds at the surface through the process of electron stimulated desorption (ESD). The dangling bonds then facilitate the adsorption of precursor resulting in film growth. Because the electron flux is directional, EE-ALD can be used for selective area deposition. For portions of the sample that are masked from the e^--beam, no dangling bonds are produced and no film growth occurs. Additionally, any portion of the surface that is parallel to the e^--beam, e.g. the walls of a trench, may be considered topographically masked because the e^--beam is not incident on the surface.

The topographically selective area deposition by EE-ALD was investigated by depositing boron nitride (BN) EE-ALD films on a trench structure. EE-ALD of BN has been demonstrated using sequential exposures of borazine ($B_3N_3H_6$) and electrons (50-450 eV) at room temperature [1]. GaN [2] and Si [3] have also been deposited earlier using EE-ALD. The topographical selectivity was investigated by growing an EE-ALD BN film on a trench structure. On the vertical walls of a trench structure, aligned parallel to the e^--beam, there should be no electron flux and no film. In contrast, the top and bottom of the trench will receive the full flux of the e^--beam. To test these ideas, high resolution TEM images were recorded after 1000 cycles of BN EE-ALD on a trench structure.

BN films were observed on the top and bottom of the trench. For the trenches used in this study, the side walls were not vertical. Some BN film deposition did occur on these sidewalls, but at a lower growth rate than the horizontal surfaces at the top and bottom of the trench. The electron flux on the side walls was reduced by a factor of $\cos\theta$ where θ is the angle between the surface normal of trench wall and the e^--beam. Incorporating the reduced electron flux into the model for EE-ALD film growth showed excellent agreement with film thicknesses observed on the trench walls. The topographic selectivity of EE-ALD, demonstrated with BN, coupled with a metal chemistry, would offer a promising solution to challenges such as the bottom-up-fill of conductors in trenches or vias.

[1] J. K. Sprenger, H. Sun, A. S. Cavanagh, A. Roshko, P. T. Blanchard and S. M. George, J. Phys. Chem. C. DOI: 10.1021/acs.jpcc.8b00796 (2018).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, Chem. Mater. 28, 5282 (2016).

[3] J.K. Sprenger, A.S. Cavanagh, H. Sun, and S.M. George, J. Vac. Sci. Technol. A. 36, 01A118 (2018).

9:20am **TF+AM+EM+PS-TuM-5 Optimization by In situ Ellipsometry of ALD and ALE Successive Steps for the Selective Atomic Layer Deposition of Ta_2O_5 on TiN and Si.***, **Vincent Pesce**, C Vallée,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R Gassilloud,* Cea Leti, France*; A Chaker, M Bonvalot, B Pelissier,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; P Nicolas,* Cea, France*; A Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The drastic reduction of microelectronic device dimensions, traditionally achieved through a photolithography process, requires more and more stringent process conditions in this top-down approach. Recent developments in atomic layer deposition processes (ALD) have shown that a new bottom-up approach is possible by the combination of ALD and Atomic Layer Etching (ALE) steps for the selective growth on patterned surfaces [1]. Indeed, it has been shown that the nucleation kinetics in the initial stages of a deposition process is strongly dependent on the chemical state of substrate surfaces. Thus, different nucleation delays can be achieved on patterned substrates, leading to significant variation of thickness in spite of a similar growth rate after nucleation (in the steady state). Prior to precursor deposition, a first step is carried out, which activates or inhibits nucleation sites on patterned substrates. For instance, an O_2/CF_4 plasma treatment leads to the formation of a fluorocarbon polymer, whose thickness depends on the chemistry of the surface: its thickness may be less on Si as compared to TiN, because SiF_4 molecules are more volatile than their TiF_4 counterparts. In turn, this CF_x rich layer can serve as a passivation layer to alter the nucleation sites during the subsequent deposition process. Similarly, an oxidation plasma treatment serves to activate nucleation sites through the formation of metal-oxygen bonds on the patterned substrate, which in turn favors an immediate growth during deposition process.

In this work, we have investigated the impact of both chemical and physical surface interactions during the deposition of Ta_2O_5 in a PE-ALD process. These investigations have been carried out in a FlexAL PEALD tool equipped with an ALE bias system developed by Oxford. A selective deposition super cycle has been defined, which consists in alternating a CF_4 plasma treatment with a Ta_2O_5 ALD deposition cycle with an O_2 plasma as oxidation step. In situ ellipsometry measurements have been used to investigate the impact of ion bombardement and the CF_x layer growth during the optimization of the ALE parameters.

These measurements have been correlated to ex situ XRR and XPS to confirm the thickness on both Si and TiN substrates and analyze the chemistry of the different layers or interfaces.

[1] R. Vallat et al. "Selective deposition of Ta_2O_5 by adding plasma etching super-cycles in plasma enhanced atomic layer deposition steps." *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 35.1 (2017): 01B104. (DOI: 10.1116/1.4965966)

9:40am **TF+AM+EM+PS-TuM-6 ALD and PEALD of ZnO on MoS_2 and WSe_2***,* ***Timothy N. Walter***[1]*, S Lee,* The Pennsylvania State Univeristy*; M Chubarov,* The Pennsylvania State University*; X Zhang,* The Pennsylvania State Univeristy*; T Choudhury, J Redwing,* The Pennsylvania State University*; T Jackson, S Mohney,* The Pennsylvania State Univeristy

Inducing nucleation on the inherently passivated surfaces of 2D materials such as transition metal dichalcogenides (TMDs) can be challenging for atomic layer deposition (ALD); however, this situation also presents an opportunity for selective growth by ALD. Additionally, ZnO/TMD heterojunctions have favorable band alignments for catalysis and offer possibilities for nanoscale electronic devices including transparent electronics, photodiodes, and piezo-phototronics. This work explores the growth of ZnO on the TMDs MoS_2 and WSe_2 using thermal ALD, thermal ALD with UV-O_3 surface pre-treatment, and plasma enhanced ALD (PEALD). Depositions were performed on both few-layer exfoliated flakes and coalesced single-layer films (with scattered 2- or 3-layer islands) that were already grown by gas source chemical vapor deposition (CVD). Samples were characterized by atomic force microscopy (AFM), Raman spectroscopy, photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS) before and after deposition of ZnO. For both MoS_2 and WSe_2, thermal ALD of ZnO using diethyl zinc (DEZ) and water at 125 °C resulted in a long nucleation delay on the TMD surfaces, showing selectivity against ZnO growth on TMDs compared to the surrounding SiO_2/Si substrate. Even after hundreds of cycles, very little change was detected by XPS, Raman spectroscopy, or AFM; however, nucleation did occur at defects and caused surface roughness to increase. UV-O_3 pre-treatment before thermal ALD yielded different results on MoS_2 compared to WSe_2. UV-O_3 functionalizes MoS_2 for nucleation and subsequent growth of ZnO without destroying the underlying MoS_2; however, UV-O_3 fully oxidized regions of the WSe_2 surface and promoted nucleation. PEALD using DEZ and N_2O on both TMDs resulted in a conformal and smooth film, but it oxidized the top layer of the TMDs according to XPS. In conclusion, UV-O_3 pre-treatment and plasma-enhanced deposition allow for nucleation and growth of ZnO on TMD substrates, sometimes to the detriment of the top layer of material; however, the planar surfaces of 2D materials resist nucleation for hundreds of cycles of thermal ALD.

11:00am **TF+AM+EM+PS-TuM-10 From Fundamental Insights into Growth and Nucleation Mechanisms to Area-selective Deposition***,* ***Annelies Delabie****,* IMEC & KU Leuven, Belgium*; J Soethoudt,* KU Leuven, Belgium*; G Pourtois, S Van Elshocht, K Barla,* Imec, Belgium*; F Grillo, E Marques, R van Ommen,* TU Delft, Netherlands **INVITED**

Area-selective deposition holds the potential to build structures from the bottom up, only where needed, with atomic precision. It is gaining importance for manufacturing of nano-electronic devices as it enables self-aligned deposition for accurate pattern placement and bottom-up deposition in trenches or holes. It can simplify complex integration flows and implies significant cost reduction. The key to area-selective deposition is surface chemistry, as it is based on the surface dependence of deposition techniques like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Today, however, only few industrial processes make use of area-selective deposition, mainly because only few materials can be deposited with sufficient selectivity. In addition, defectivity is a great challenge, as substrate inhibition is often associated with island growth. Detailed insights into the surface chemistry and nucleation mechanisms is essential, as this insight can be used to expand the material combinations accessible by area-selective deposition, as well as to design defect removal strategies. Finally, area-selective deposition is affected by patterning due to changes in surface composition and/or due to diffusion. This illustrates the need for understanding and optimization of the processes in patterns with relevant dimensions. In this work, we review our current understanding of the inherent surface dependence of ALD processes. We show how insight into the growth and nucleation mechanisms of ALD can be applied to enable area-selective deposition with defect removal solutions.

11:40am **TF+AM+EM+PS-TuM-12 DETA SAMs as ALD Ru Inhibitor for Area-selective Bottom-up Interconnects***,* ***Ivan Zyulkov,*** IMEC & KU Leuven*; S Armini,* IMEC, Belgium*; S De Gendt,* IMEC, KU Leuven, Belgium

Replacement of Cu interconnects by an alternative metal will be required beyond 32 nm metal pitch in order to decrease the metal line resistance and prevent IC failure due to the Cu electromigration. Based on recent studies, Ru has several advantages when compared to Cu, which make it an attractive candidate for the Cu replacement: i) lower thickness dependence of the resistivity due to a short electron mean free path (6.6/4.9 nm for Ru vs 39.9 nm for Cu), ii) higher melting temperature (2334 ºC for Ru vs 1032 ºC for Cu) which represents better Ru resistance to electromighration and iii) possibility of integration without a diffusion barrier, resulting in a larger effective metal area. However, conventional electrochemical and electroless deposition methods used in IC manufacturing are not available for the Ru metallization. Additionally, downscaling of the metal structures down to 10 nm causes metal lines filling issues even using conformal ALD, since seams are likely to be formed due to trench pinch-off. As a solution, area selective deposition (ASD) can be exploited, allowing bottom-up and void-free filling of high aspect ratio structures. In addition, ASD of Ru can find application in advanced patterning schemes.

This work is focused on ASD of Ru in a via area of the interconnect structure. In this case ALD selectivity to metallic via bottom (underlying metal line) should be achieved with respect to organosilicate glass (OSG) via sidewalls. In this work, thermal ALD Ru using an ethylbenzene-ethyleyelohexadiene (EBECHRu) precursor with O_2 co-reactant was used. The precursor molecule has ethyl-cyclohexadienyl ligands, which are expected to show a preferential interaction/ inhibition with specific surface groups. In order to passivate the hydroxy-terminated OSG sidewalls against the Ru deposition different siloxane derived self-assembled monolayers (SAMs) were used. According to RBS and SEM analysis, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) SAMs provide more than 300 cycles inhibition of the ALD Ru growth on Si oxide and OSG. XPS, FTIR and spectroscopic ellipsometry on the SAM film before and after ALD are compared in order to identify relevant selectivity mechanisms. In order to prevent DETA passivation of the Cu interface where ALD Ru is expected to grow for the bottom-up via fill, undecanethiol (UDT) SAMs were used as a selective sacrificial Cu protection before the DETA deposition. The thiol SAMs can be removed from the Cu surface at 250 ºC while silane (DETA) is stable on the dielectric surface at temperatures above 350 ºC and higher. The double SAM and area selective bottom-up ALD Ru tested in 45 nm half-pitch lines will be presented.

---

[1] **TFD James Harper Award Finalist**

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+MI+MN+SS+TR-TuA

SPM – Probing and Manipulating Nanoscale Structures

Moderators: Renu Sharma, NIST Center for Nanoscale Science and Technology, Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **NS+AM+MI+MN+SS+TR-TuA-1 Building Artificial Quantum Matter with Dopant Atoms*, Sven Rogge,*** University of New South Wales, Australia **INVITED**

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a “semiconductor vacuum” for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

3:00pm **NS+AM+MI+MN+SS+TR-TuA-3 Scanning Tunneling Microscopy Study of Structure Control of a Nanocarbon Catalyst through a Surface-Activated coupling Reaction*, Jeremy Schultz,*** *P Whiteman, N Jiang,* University of Illinois at Chicago

In order to optimize nanocarbon materials for metal-free catalysis, the structure must be controlled and characterized at the nanoscale. One method for the bottom-up assembly of nanocarbon catalysts is through an Ullmann-type coupling reaction induced by a metal substrate, where a halide leaving group allows covalent intermolecular coupling. Scanning tunneling microscopy has been applied to a fundamental study of 3,6-dibromo-phenanthrequinone (DBPQ), a molecule selected for its catalytically active diketonic groups. Conjugated polymers formed from DBPQ have been found to be capable of catalyzing alkane oxidative dehydrogenation (ODH) reactions as well as nitrobenzene (NB) reduction reactions.

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA-4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM*, Songbin Cui,*** Pohang University of Science and Technology, Republic of Korea*; U Ham,* Institute for Basic Science (IBS), Republic of Korea*; T Kim,* Pohang University of Science and Technology, Republic of Korea

Photon signal can be enhanced significantly by modifying the plasmonic nanocavity. This enhancement becomes an important issue in super-resolution microscopy and high resolution spectroscopy, such as scanning tunneling microscopy (STM) electroluminescence [1], surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy [2], and so on. Low temperature STMs can allow us to achieve less than 1nm tip-sample gap stably. This gap-mode plasmonic nanocavity between an STM tip and surface realizes sub-molecular photon spectroscopy [1]. A few works demonstrated that light emission signal can be effectively enhanced by certain resonant plasmonic spectral peaks, which can be modified by tip indentation [2] and showed theoretically that the larger tip aperture causes a blue shift and the shaper apex curvature results in higher intensity in a photon spectrum [3]. However, the tip shape dependence of the plasmonic nanocavity remains unclear. In this work, we experimentally present the role of tip shape in surface plasmonic light emission. We have used Ag tips and a Ag(100) substrate, and photon signals have been measured from both side of the STM tip simultaneously. We dipped STM tips into the substrate with controlling the dipping depth and the lifting speed in order to change the tip shape, and then, the tip shape subsequently was checked through STM profiles. We found that changing small parts of tip apex (<3nm tip direction) can differ the photon spectrum significantly. Furthermore, the plasmonic photon emission from different direction from a STM tip could be quite different due to tip shape asymmetry. This finding can help us to tune the plasmonic photon emission spectra more efficiently.

[1] R. Zhang et al., Nature 498, 82–86 (2013).

[2] Z. C. Dong et al., Nature Photonics 4, 50–54 (2010).

[3] J. Aizpurua et al., Physical Review B 62, 2065-2073 (2000).

4:20pm **NS+AM+MI+MN+SS+TR-TuA-7 Advances in SPM Methods for Energy-relevant Materials*, Marina Leite,*** University of Maryland College Park **INVITED**

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group’s recent research discoveries based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage Voc > 300 mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the Voc in perovskite solar cells with spatial resolution < 100 nm. Unexpectedly, we identify a ‘residual Voc’ post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

[1] *ACS Energy Letters* **2**, 2761 (2017). Invited Review.

[2]*ACS Energy Letters* **2**, 1825 (2017). Invited Perspective

[3] *Nano Letters***17**, 2554 (2017).

[4] *ACS Energy Letters***1**, 899 (2016).

[5] *Advanced Energy Materials* **5**, 1501142 (2015).

5:00pm **NS+AM+MI+MN+SS+TR-TuA-9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon*, Chuanxu Ma,*** *L Liang,* Oak Ridge National Laboratory*; Z Xiao,* North Carolina State University*; A Puretzky, K Hong,* Oak Ridge National Laboratory*; W Lu, J Bernholc,* North Carolina State University*; A Li,* Oak Ridge National Laboratory

High quality electrical contact to low-dimensional semiconductor channel materials is the key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Inappropriate contacts create interfacial states that can pin the Fermi level and form a large Schottky barrier. For 2D transition metal dichalcogenides (TMDs), a route to a high-performance contact has recently been proposed by using a phase transition that converts a hexagonally packed semiconductor (2H) phase into a distorted octahedrally packed metallic (1T’) phase. However, a similar approach is not available for 1D materials. Conceptually, an ideal contact would be a metal-semiconductor interface formed with native covalent bonds without introduction of any structural or electronic boundaries. Realization of such a seamless contact in 1D materials such as graphene nanoribbons (GNRs) requires atomically precise development of a heterostructure from well-defined atomic or molecular precursors.

Here we report on a successful approach for making seamless contacts in 1D materials through the formation of GNR staircase heterostructure. The coherent staircase is made of GNRs with widths varying from 7, 14, 21 and up to 56 carbon atoms. The graphitic heterostructures are synthesized by a surface-assisted self-assembly process with a single molecular precursor. While the 7-atom-wide GNR is a large-gap semiconductor, the conjugated wide GNRs are either quasi-metallic or small-gap semiconductors, similarly to the 2D metals. Our study, which combines STM and Raman measurements with DFT calculations, reveals that the heterointerface consists of native sp^2 carbon bonds without localized interfacial states. Such a seamless heterostructure offers an optimal electrical contact to the wide-gap 1D semiconductor.

5:20pm **NS+AM+MI+MN+SS+TR-TuA-10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy***, **MinHui Chang,*** Korea University, Republic of Korea*; Y Chang, N Kim,* Korea Advanced Institute of Science and Technology (KAIST)*; U Jeon, H Kim,* Korea University, Republic of Korea*; Y Kim,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; S Kahng,* Korea University, Republic of Korea

Binding reaction between small molecules and metallo-porphyrins play crucial roles in functional processes of biological systems such as oxygen delivery, muscle contraction, and synaptic transmission. Their geometrical structures such as tilted binding of NO to metallo-porphyrin have been recently confirmed by high-resolution scanning tunneling microscopy (STM) images at the single molecule level. Here, we present STM images of further systems, di, tri, and quadra-atomic small molecules, coordinated to metallo-porphyrin on Au(111). We observed square ring, rectangular ring, and center-bright structures for three different small molecules. With the help of density functional theory (DFT) calculations, we reproduce the experimental STM images in the simulated images. Thus, our study shows that geometric structures of small molecules coordinated to metallo-porphyrins can be probed with STM combined with DFT methods.

5:40pm **NS+AM+MI+MN+SS+TR-TuA-11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers***, **Dominic Goronzy**[1], E Avery, N Gallup,* University of California, Los Angeles*; J Staněk, J Macháček, T Baše,* Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic*; K Houk,* Chemistry and Biochemistry, University of California, Los Angeles*; P Weiss,* University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers *via* STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a pK_a of 3-3.2 in solution (3D) to an apparent surface pK_a of approximately 6.5-7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in pK_a consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the pK_a shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to explore dimensionality effects in biological systems, including proteins confined within membranes.

---

[1] **NSTD Student Award Finalist**

Extending Additive Manufacturing to the Atomic Scale Focus Topic
Room Hall B - Session AM-TuP

Extending Additive Manufacturing to the Atomic Scale Poster Session

AM-TuP-1 Direct-Write Fabrication of 3D Nano-Probes for Thermal Microscopy, *J Sattelkow, J Froech, R Winkler,* Graz University of Technology, Austria*; C Schwalb, E Fantner,* GETec Microscopy Inc., Austria*;* ***Harald Plank,*** Graz University of Technology, Austria

With the recent introduction of controlled 3D nano-printing via focused electron beam induced deposition (FEBID), entirely new ranges of applications such as nano-optics, –sensors, -magnetics or -mechanics comes within reach whose fabrication is extremely challenging or even impossible with alternative techniques. In this study, we use 3D FEBID for the direct-write fabrication of thermal 3D nano-probes for further application in Scanning Thermal Microscopy (SThM). In more detail, freestanding Pt–C multi-branch architectures are used as thermistors, where the electric bridge resistivity changes in dependency on local temperatures during SThM. The main advantage of this nano-bridge concept is the small volume in the tip merging zone together with end radii down to 5 nm, which enable fast thermal response and high lateral resolution, respectively.

First, the relations between multi-branch design and nano-mechanical properties are studied by a combined approach of finite element simulations, Atomic Force Microscopy (AFM) based force spectroscopy and real-time imaging via scanning electron microscopy. This not only leads to identification of ideal overall geometries but also reveals the high demands on fabrication accuracy to minimize unwanted morphological twisting and non-linear mechanical behavior under force load. In the second step, we introduce a material tuning approach via post-growth e-beam curing, which effectively transforms the carbon matrix around the Pt nano-grains into sp^3 hybridized 3D carbon networks. This not only increases the overall mechanical stability but in particular improves the wear resistance of the tip apex for stable AFM imaging. In the final step, we use FEBIDs direct-write capabilities to modify pre-structured AFM cantilevers by fully optimized 3D nano-probes for active thermistor operation via monitoring the electric current through the 3D nano-bridges. Thermal response studies in ambient and vacuum conditions are presented and demonstrate temperature sensitivities with sub-degree resolution as well as response times better than 32 ms/K for dynamic thermo-studies

AM-TuP-2 Laser Induced Formation of Eutectic Nanostructures in Al-Cu Powder for Additive Manufacturing, ***Jonathan Skelton****, C Headley, J Floro, J Fitz-Gerald,* University of Virginia

With the emergence of additive manufacturing (AM) via laser powder bed sintering, design of the starting powders represents a critical area of interest, dictating the final properties of the AM components a large degree. The ability to design the nanoscale physical structure within powder particles in order to improve the final properties (optical, mechanical, thermal) remains a challenge. This research investigates the change in the eutectic microstructure of Al-Cu powders following laser irradiation. The initial powder alloy (gas atomized, Al-33wt%Cu) exhibited a variety of eutectic microstructures due to the varying solidification rates of particles within the gas atomized process. As-received powder was annealed at 450°C for 2 hours so as to create a uniform, $Al+Al_2Cu$ two-phase structure with an interphase periodicity of about 2 µm. The original lamellar eutectic is broken down into a more irregular structure as part of the coarsening process. The powder, mounted on a glass slide and within an air ambient, is then subject to pulsed laser irradiation (wavelength = 248 nm, pulse duration 25 ns, fluence of 1.5 J/cm^2). Irradiation melted the particles, creating a new eutectic solidification structure with lamellar morphology. The interphase spacing was reduced to 30 nm, indicative of rapid solidification. Due to the lack of wetting or sintering between particles, it was concluded that each particle was melting and solidifying within its respective oxide shell. Though particles retain a largely spherical shape, many particles displayed a collapsed or partially "deflated" morphology after laser irradiation. The origin of the deformed morphology is not understood, but does not appear to be a phenomenon strictly associated with an instability imposed by the pulsed irradiation. It is suspected that the rapid growth and deflation of the oxide shell due to the thermal expansion of the Al-Cu particles may play a role. Samples were characterized by scanning electron microscopy (SEM), dual beam focused ion beam (DB FIB), and x-ray photoelectron spectroscopy (XPS). Support of the National Science Foundation through grants CMMI-1663085 is gratefully acknowledged.

2D Materials Focus Topic
Room 201B - Session 2D+AM+EM+NS-WeM
Dopants, Defects, and Interfaces in 2D Materials

Moderator: Eric Pop, Stanford University

8:00am **2D+AM+EM+NS-WeM-1 Carbon Doping of 2D Transition Metal Dichalcogenides by Plasma Enhanced CVD*, Yanfu Lu*,** *F Zhang, S Sinnott, M Terrones,* The Pennsylvania State University

Doping of 2D transition metal dichalcogenides has been discovered to be an effective way to tune the electronic structure and modify the lattice structure at the surface. The n-type and p-type doping of monolayer MoS_2/WS_2 heterostructures may enable the fabrication of field-effect transistors of ultra-low thickness. Plasma enhanced chemical vapor deposition provides a stable and controllable approach for introducing carbon dopants to monolayer WS_2. Photoluminescence measurement indicates that the band gap of C-doped WS_2 decreases by 0.17 eV. Corresponding first principles calculations provide the correlation between the position and chemical saturation of the carbon dopants and the electronic structure of the system. To verify covalently bonded dopants, we use Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning transmission electron microscopy to examine the pristine sample and carbon-doped samples. Subsequent I-V characteristics measurements prove p-type doping and the energy band diagram. Finally, the mechanism associated with and, more importantly, the structure-property relationship of chalcogen doping are analyzed. The resulting new insights of transition metal dichalcogenide-based heterostructures and alloys are discussed.

8:20am **2D+AM+EM+NS-WeM-2 Methoxy Formation Induced Defects on MoS_2****, ***Duy Le,*** University of Central Florida*; P Evans,* University of Nebraska - Lincoln*; Z Hooshmand,* University of Central Florida*; T Rawal,* Oak Ridge National Laboratory*; L Bartels,* University of California, Riverside*; P Dowben,* University of Nebraska-Lincoln*; T Rahman,* University of Central Florida

Defects are known to play an important role in determining the chemical properties of otherwise inert MoS_2 basal plane. Here we report our joint experimental and theoretical study of the adsorption and reaction of methanol on the MoS_2 basal plane to determine the factors that control system reactivity. We find that exposure of the MoS_2 basal plane to methanol leads to the formation of adsorbed methoxy and coincides with sulfur vacancy generation and that the methoxy moieties bind to molybdenum, not sulfur, while some adsorbed methanol is readily desorbed near or slightly above room temperature. Our calculations also suggest that the dissociation of methanol via O–H bond scission occurs at the defect site (sulfur vacancy), followed subsequently by formation of a weakly bound H_2S species that promptly desorbs from the surface with creation of a new sulfur vacancy, in great agreement with photoluminescence and scanning tunneling microscopy data that show clear evidence of the sulfur vacancy creation on the MoS_2 surface, after exposure to methanol [1].

[1] P. Evans et al, J. Phys. Chem. C (2018). DOI: 10.1021/acs.jpcc.8b02053

* Work supported in part by DOE grant DE-FG02-07ER15842

8:40am **2D+AM+EM+NS-WeM-3 Defect Engineering of 2D Materials for Advanced Electronic Devices*, Gwan-Hyoung Lee,*** Yonsei University, Republic of Korea **INVITED**

Two-dimensional (2D) materials have brought a great deal of excitement to nanoscience community with their attractive and unique properties. Such excellent characteristics have triggered highly active researches on 2D material-based electronic devices. New physics observed only in 2D semiconductors allow for development of new-concept devices. Assembly of 2D blocks for van der Waals heterostructures also provide a big playground for engineers and physicists to investigate unprecedented properties of 2D materials and fabricate multi-functional electronic devices. However, atomically thin 2D materials, such as graphene and transition metal dichalcogenides (TMDs), have only two surfaces at top and bottom without a bulk so that they are very sensitive to environment. In other words, properties of 2D materials can be altered easily by surface modification. In this talk, I will show novel approach to fabricate high performance 2D electronic devices by utilizing various surface treatments, such as fluorination and hydrogenation of graphene and layer-by-layer oxidation of MoS_2. When different types of defects, such as *sp*^{3} bonds and vacancies, are induced on the surface of graphene, the electrical properties of graphene can be tuned. With mild plasma treatment, MoS_2 can be oxidized layer-by-layer and monolayer MoS_2 can be fabricated from the multilayer MoS_2. These surface treatment techniques can be used for fabrication of high performance graphene devices and MoS_2 optoelectronic devices. Defect engineering of 2D materials holds a great promise in engineering the 2D materials and fabricating advanced electronic devices of 2D materials.

9:20am **2D+AM+EM+NS-WeM-5 Modeling Defects and Electron-electron Interactions in Low-dimensional Materials*, Daniel Gunlycke,*** *C Ekuma,* U.S. Naval Research Laboratory

While each nanoscale structure in a low-dimensional material can exhibit a variety of properties, the odds are that it will be (1) sensitive to defects and (2) strongly influenced by electron-electron interactions. The ratio of defect sites to pristine sites naturally increases, as structures become smaller. Electron localization can furthermore dramatically magnify the role of defects. In low-dimensional materials, dielectric screening is generally less effective, reducing the tendency for electronic interactions to become uniform across the sites in the materials. Despite the importance of both defects and electron-electron interactions, the properties of low-dimensional materials are often investigated in the absence of one or the other. This not only creates uncertainty over the predictions but could entirely miss certain physical phenomena, including insulator-to-metal transitions. In this presentation, we will discuss a general first-principles-based approach to explore realistic low-dimensional structures that explicitly accounts for both defects and electron-electron interactions [1]. It is based around a generalized Anderson Hamiltonian and applies density functional theory, as well as dynamical mean-field theory. We will also present electronic and optical properties of two-dimensional materials obtained using our method and discuss the potential for using defect engineering for improved solar cell performance.

[1] C. E. Ekuma, V. Dobrosavljevic, and D. Gunlycke, *Physical Review Letters* **118**, 106404 (2017)

This work was supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

9:40am **2D+AM+EM+NS-WeM-6 Post-Synthesis Modifications of Two-Dimensional $MoSe_2$ or $MoTe_2$ by Incorporation of Excess Metal Atoms into the Crystal Structure*, Paula Mariel Coelho*,** University of South Florida*; H Komsa,* Aalto University, Finland*; H Coy Diaz, Y Ma,* University of South Florida*; A Krasheninnikov,* Institute of Ion Beam Physics and Materials Research, Germany*; M Batzill,* University of South Florida

Modifications of $MoSe_2$ and $MoTe_2$ with metallic mirror twin grain boundaries (MTB) in films grown by molecular beam epitaxy have been previously reported [1,2]. The goal of the study presented here has been to understand the formation-mechanism of MTB networks and apply this gained knowledge for controlled modifications of these 2D materials. In a combined scanning tunneling microscopy and density functional theory approach we demonstrate that excess Mo can easily diffuse into the pristine $MoSe_2$ or $MoTe_2$ (but not into MoS_2) layer and cause crystal modifications into Mo-rich twin grain boundaries. Vapor deposited Mo atoms are first incorporated by diffusing into interstitial (or split-interstitial) sites. Then, further Mo-atoms incorporate into the crystal structure to form triangular, Mo-rich grain boundary loops. Only after a critical density of MTBs is reached, Mo is no-longer absorbed by the 2D-crystal sheet and Mo-clusters start to form at the surface. The energetics and barriers for Mo-incorporation is calculated by DFT and shows that the formation of twin grain boundaries in the presence of excess Mo is favorable for $MoTe_2$ and $MoSe_2$, but not for MoS_2 - in agreement with the experiment. The achievable dense networks of MTBs constitute a new Mo-rich metallic phase that may be used for controlled electric contacts or creation of active sites in electro-catalysis [4] and thus adding new functionalities into transition metal dichalcogenide-based materials and devices. Moreover, DFT simulations suggest that this mechanism for incorporation of transition metals is not limited to Mo. This enables modification of the materials properties by heteroatom dopants and initial experimental work demonstrates the incorporation of both Ti and V. V-interstitials in $MoTe_2$ are predicted to have a magnetic moment and magnetic hysteresis curves indicate the induction of ferromagnetism in $MoTe_2$ by doping the material with less than 1% of V interstitials.

REFERENCES:

[1] Ma Y, et al. (2017) Metallic Twin Grain Boundaries Embedded in $MoSe_2$ Monolayers Grown by Molecular Beam Epitaxy. *ACS Nano* 11, 5130-5139.

[2] Coy Diaz H, Ma Y, Chaghi R, Batzill M. (2016) High Density of (Pseudo) Periodic Twin-Grain Boundaries in Molecular Beam Epitaxy-Grown van der Waals Heterostructure: $MoTe_2$/MoS_2. *Appl. Phys. Lett.* 108, 191606.

[3] Ma Y. et al. (2017) Angle resolved photoemission spectroscopy reveals spin charge separation in metallic MoSe2 grain boundary. Nat. Commun. 8, 14231.

[4] Tomasz Kosmala et al. (2018) Metallic Twin Boundaries Boost the Hydrogen Evolution Reaction on the Basal Plane of Molybdenum Selenotellurides. *Adv. Energy Mater.* 2018, 1800031.

11:00am **2D+AM+EM+NS-WeM-10 Dry Cleaning and Doping of MX_2 for Contact Engineering***, **Daniil Marinov,*** IMEC, Belgium*; J Ludwig,* IMEC & KU Leuven, Belgium*; D Chiappe,* IMEC, Belgium*; E Voronina, T Rakhimova,* Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University*; J de Marneffe, I Asselberghs,* IMEC, Belgium*; S De Gendt,* IMEC, KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (e.g. MoS_2, WS_2) are promising materials for a number of electronic and optoelectronic applications. Wafer-scale integration of these materials into sophisticated devices requires atomic-scale control of the processing steps such as deposition, etch, clean and doping. Reduction of the contact resistance is a major roadblock towards demonstration of high-performance devices. Significant Schottky barrier at the metal-MX_2 interface as well as surface contamination (e.g. by polymer residues) are the main factors contributing to the high contact resistance in fabricated MX_2 devices. In this study, a fully dry cleaning and doping technique is developed with a particular focus on contact engineering.

We demonstrate that a remote H_2 plasma is efficient for removal of organic residues from MX_2 surfaces. However, sulfur can be also stripped from the topmost layer by reactive H atoms. The main challenge is thus to precisely control the sulfur loss while maintaining the cleaning efficiency. At high substrate temperature, a 200 nm PMMA layer can be fully removed selectively to a single layer of WS_2 without damaging the 2D material (as confirmed by photoluminescence measurements). At low substrate temperatures significant S-vacancy formation was observed. Surface temperature is therefore the key parameter for controlling the reactivity of H atoms on WS_2.

Controllable formation of sulfur vacancies opens routes for substitutional doping. After H_2 plasma strip, WS_2 and MoS_2 samples were exposed to a flow of molecular gases (Cl_2, CO, OCS) without igniting the plasma. It is shown that Cl_2 and OCS can react with H_2 plasma treated MX_2 forming stable surface groups. Ex-situ conductive AFM measurements confirm that molecular doping prevents the loss of conductivity (that is observed after H_2 plasma alone). Moreover, OCS and Cl_2 exposure enhances electrical current injection in the material through grain boundaries and edges. The latter effect is beneficial for contact resistance reduction on MX_2.

To gain a deeper insight in the observed surface phenomena, DFT simulation of the interaction of atomic (H, Cl, F) and molecular (OCS, Cl_2) species with MX_2 surface was performed. S-vacancy creation by atomic hydrogen via formation of gas phase H_2S was observed in simulations, in qualitative agreement with the experiments. Moreover, dissociative adsorption of Cl_2 and OCS in S-vacancy sites is predicted by the DFT model.

Dr D. Marinov has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 752164.

11:20am **2D+AM+EM+NS-WeM-11 Deep Learning for Atomically-Resolved Scanning Transmission Electron Microscopy Experiments on 2D Materials***, **Maxim Ziatdinov,*** *S Kalinin,* Oak Ridge National Laboratory

Understanding fundamental atomic-scale mechanisms behind solid state reactions and phase transformations is critical for optimizing functional properties of technologically relevant materials. Recent advances in scanning transmission electron microscopy (STEM) have allowed to visualize dynamic processes in solid state systems, induced by thermal or chemical stimuli or electron beam, on the level of individual atoms and single atomic defects. However, while there have been multiple STEM studies on materials structure evolution, the materials-specific knowledge on the kinetics and thermodynamics of these processes and atomic potentials is almost non-existent, which is mainly due to the inherent limitations of the current (semi-)manual image analysis techniques. Here we demonstrate an approach based on deep convolutional neural networks for automated analysis of dynamic STEM data from 2-dimensional materials, such as monolayer WS_2, under e-beam irradiation. Our approach allows to create a library of atomic defects, explore subtle atomic distortions around the defects of interest and map chemical transformation pathways on the atomic level. We specifically show how the developed framework can be used for extracting diffusion parameters of sulfur vacancies in WS_2 and for studying transformation pathways for Mo-S complexes, including detailed transition probabilities.

11:40am **2D+AM+EM+NS-WeM-12 Magnetic Doping in 2D MBE-grown-$MoSe_2$/graphene Heterostructures Studied by Photoelectron Spectroscopy and Band Structure Imaging***, **Maxime Gay,** O Renault,* CEA-LETI, France*; M Dau, C Vergnaud, M Jamet,* CEA-INAC-SPINTEC, France

2D TMDCs present a unique combination of electronic and mechanical properties such as a direct bandgap, strong spin-orbit coupling and K-valley inequivalence, with an atomic-scale thickness [1]. Introducing magnetic phases into these materials opens exciting perspectives towards spin control in magnetic tunnel junctions. To date, magnetism in 2D systems was mostly studied by theoretical calculations. Within the diluted magnetic semiconductors model, transition metal atoms from the monolayer are substituted by a few Mn, Fe or Co atoms [2-4].

Our study focuses on Mn-doped-$MoSe_2$ monolayers, grown by molecular beam epitaxy on graphene, and characterized by photoemission techniques (XPS, kPEEM) coupled with observations at different scales (DRX, TEM). Before doping, we found that the in-plane lattices of graphene and $MoSe_2$ are aligned with each other and that a bandgap opens in the graphene around the Fermi level [5-6]. After Mn doping, the obtained Mn insertion is measured up to 15% by XPS. The influence of Mn doping on the band structure of $MoSe_2$/graphene heterostructure will be presented and discussed.

REFERENCES

[1] Manzeli, S., et al. Nat. Rev. Mater. 2, 17033 (2017).

[2] Mishra, R., et al. Phys. Rev. B - Condens. Matter Mater. Phys. 88, 1–5 (2013).

[3] Zhang, K., et al. Nano Lett. 15, 6586–6591 (2015).

[4] Singh, N. & Schwingenschlögl, U. ACS Appl. Mater. Interfaces 8, 23886–23890 (2016).

[5] Dau, M. T., et al. Appl. Phys. Lett. 110, 11909 (2017).

[6] Dau, M. T., et al. ACS Nano 12, 3, 2319-2331 (2018).

Extending Additive Manufacturing to the Atomic Scale Focus Topic
Room 102B - Session AM+NS+SS-WeM

Nanofabrication with Focused Electron Beams (8:00-10:00 am)/Atomic Scale Manipulation with Focused Electron Beams (11:00 am-12:20 pm)

Moderator: Ondrej Dyck, Oak Ridge National Laboratory

8:00am **AM+NS+SS-WeM-1 3D Nano-Printing via Focused Electron Beams: An Emerging Technology for Novel Applications***, **Harald Plank,** R Winkler, J Sattelkow,* Graz University of Technology, Austria*; J Fowlkes,* Oak Ridge National Laboratory*; P Rack,* University of Tennessee Knoxville **INVITED**

3D-printing of functional structures has emerged as an important technology in research and development. While being reliable on the micro and sub-micron scale, the extension to the nanoscale is still a challenging task. Among the very few direct-write techniques on that scale, focused electron beam induced deposition (FEBID) is one of the promising candidates as this technology allows fabrication of functional nano-structures on almost any material and substrate morphology in a single-step process. Based on strong fundamental progress in recent years, FEBID was demonstrated to be capable of fabricating complex, freestanding 3D nano-architectures with individual branch diameters down to 20 nm. Together with the increasing availability of precursors with different functionalities, FEBID is advancing from a versatile research tool into a predictable and reliable 3D nano-printer, which opens up new opportunities for advanced applications.

In this contribution, we start with the basic principles of 3-dimensional printing via FEBID, complemented by simulations for deeper insight into the fundamental processes that are operative. In the following, we present a variety of 3BID based proof-of-principle studies to demonstrate the capabilities of this direct-write technology. This ranges from scientifically oriented applications, such as plasmonics, magnetics and nano-mechanics toward industrially relevant concepts for scanning probe microscopy related tip fabrication, such as electrical, thermal and optical 3D nano-probes. Finally, we overview some of the remaining challenges and provide an outlook on future activities.

8:40am **AM+NS+SS-WeM-3 3D Nanoprinting using an Electron Beam: Simulations and Computer-aided Design**, ***Jason Fowlkes,*** Oak Ridge National Laboratory*; R Winkler,* Graz Centre for Electron Microscopy, Austria*; B Lewis,* Carl Zeiss Microscopy, LLC*; A Fernandez-Pacheco, L Skoric, D Sanz-Hernandez,* University of Cambridge*; M Stanford, E Mutunga, P Rack,* University of Tennessee*; H Plank,* Graz University of Technology, Austria **INVITED**

The deposition of complex 3D nanoscale objects with prescribed geometry and function constitutes a major goal of nanoscience. Additive assembly is the ideal approach to efficiently deposit 3D materials. Focused electron beam induced deposition (FEBID) is a resist-free, direct–write method suitable for the additive deposition of materials on both planar and nonplanar surfaces. During FEBID, a focused electron beam is scanned along the substrate surface inducing the deposition and condensation of absorbed precursor molecules, often an organometallic, delivered locally by an in-situ gas injector. Until recently, 3D deposition using FEBID was mostly a trial-and-error exercise lacking a reliable framework to deposit a wide range of geometries.

A design environment specific to beam induced deposition will be presented that has enabled the deposition of complex, 3D nanoscale mesh style objects spanning nanometer to micrometer length scales. A complementary 3D simulation of FEBID provides a predictive capability that aides in the design of more complex 3D deposits. The purpose of this design/simulation capability is to generate the primary electron beam coordinates and beam exposure dwell times necessary for the experimental deposition of 3D mesh objects, with a reduced fill factor, i.e., geometries required for the design of metamaterials, high–aspect ratio sensors/actuators and/or nanomagnetic/optical lattices.

The simulation reveals that precursor surface diffusion and electron beam induced heating, in particular, can impose unwanted mesh object distortions if not properly accounted for. This general rule applies for several precursors under picoampere, millisecond beam exposure using typical local precursor fluxes consistent with high vacuum scanning electron microscope operation. Compensation for these influences can be applied in either the CAD phase, as geometric distortions, or through the introduction of exposure pulsing which acts to mitigate the development of transient mass/heat gradients. The role of simulation in design will also be explained in the context of the proximity effect due to scattered electrons, specifically their role in inducing unwanted deposition. Simulation results are limited to cases where complementary experiments converge with simulated predictions in terms of the final deposit geometry and the electrical current collected dynamically during deposition.

9:20am **AM+NS+SS-WeM-5 2D/3D Nano-printed Functional Structures for Application and Device Development using Focused Electron Beams**, ***Michael Huth,*** Institute of Physics, Goethe University, Frankfurt am Main, Germany **INVITED**

Focused electron beam induced deposition (FEBID) is a direct-write method for the fabrication of nanostructures whose lateral resolution rivals that of advanced electron beam lithography but is in addition capable of creating complex three-dimensional nano-architectures even on non-standard materials and surfaces. In FEBID, a precursor gas adsorbed on a substrate surface inside of a scanning electron microscope is dissociated in the focus of the electron beam. This implies a conceptual similarity to „conventional“ 3D printing. However, more than anything else it is the intrinsic material properties of FEBID structures which give this technique its particular strength and relevance when compared to other nano-fabrication approaches. In this regard, the realization of novel, custom-tailored sensor concepts is exemplary for the various developments in FEBID that led to a growing number of scientific contributions in solid state physics and materials science over the last decade.

In this talk an overview is given of the application of FEBID structures for nano-sensing of force and strain, dielectric changes or charge accumulation in the environment of the sensor element, as well as magnetic stray fields. Single-electron charging and proximity to a metal-to-insulator transition form a common ground from which the design and realization of a desired sensor functionality are accomplished, as is the possibility to finely tune the sensor’s signal-to-noise ratio *in situ*.

The essential part of the sensor functionality based on FEBID structures is the microstructure that results if metal-organic precursors are used in the writing process. In many instances, *nano-granular metals* result, i.e., nanometer-sized metallic particles are formed that are embedded in an insulating matrix. Charge transport in nano-granular metals is dominated by tunneling. From this it is apparent that they might be suitable materials for strain-sensing since the tunnel coupling has an exponential dependence on the inter-grain distance which is altered under strain. However, charge transport in nano-granular metals does not only depend sensitively on the inter-grain distance. The average grain size and the dielectric properties of the insulating matrix as well as the material properties in close proximity to the nano-granular metal are equally important. The corresponding electronic parameters that determine the charge transport regime are the inter-granular tunnel coupling, the charging energy of a single grain and the dielectric function of the matrix material. It is the interplay of these parameters and their tunability that leads to the large application domain of FEBID-based sensing.

11:00am **AM+NS+SS-WeM-10 Single Atom Scale Manipulation of Matter by Scanning Transmission Electron Microscopy**, ***Stephen Jesse****, O Dyck, S Kalinin,* Oak Ridge National Laboratory **INVITED**

Fabrication of atomic scale structures remains the ultimate goal of nanotechnology. The reigning paradigms are scanning probe microscopy (SPM) and synthesis. SPM assembly dates to seminal experiments by Don Eigler, who demonstrated single atom manipulation. However, stability and throughput remain issues. The molecular machines approach harnesses the power synthetic chemistry to build individual functional blocks, yet strategies for structural assembly remain uncertain.

In this presentation, I discuss research activity towards a third paradigm — the use of the atomically focused beam of a scanning transmission electron microscope (STEM) to control and direct matter on atomic scales. Traditionally, STEM’s are perceived only as imaging tools and beam induced modifications as undesirable beam damage. Our team and several groups worldwide have 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 the atomic level, and demonstrate how beam control, rapid image analytics, better insight through modelling, and image- and ptychography based feedback allows for controlling matter on atomic level.

This research is supported by and performed at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

11:40am **AM+NS+SS-WeM-12 Single Atom Modification of 2D Materials: Fabrication and Electronic Structure**, ***Demie Kepaptsoglou,*** *F Hage,* SuperSTEM Laboratory, UK*; T Susi, J Kotakoski, J Meyer,* University of Vienna, Austria*; Y Lin, K Suenaga,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T Hardcastle,* University of Leeds, UK*; U Bangert,* University of Limerick, Republic of Ireland*; J Amani, H Hofsaess,* University of Göttingen, Germany*; Q Ramasse,* SuperSTEM Laboratory, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

The past decade has seen incredible progress in the ability to isolate and manipulate two-dimensional crystals. Due to their unique structure and dimensionality, it is possible to confine charge carriers in two dimensions, resulting in peculiar physical, chemical and electronic properties. Such novel properties can be further controlled and tuned through defects such as single atom dopants, interfaces, etc. This defect engineering takes place quite literally at the atomic level, where a combination of low voltage scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and *ab-initio* calculations provides not only the most powerful means of characterization, but also a unique tool for manipulating the single atom structures and engineer their electronic interaction with the host matrix. This approach was recently used to demonstrate that low energy ion implantation (of dopants such as N and B) can be successfully implemented to introduce single substitutional defects with excellent retention rates and without affecting the structural integrity of the surrounding graphene matrix. Atomically-resolved EELS experimental data reveals the bonding signature of the dopants themselves and their impact on the surrounding lattice. *Ab initio* calculations, in excellent agreement with the experiment, confirm the nature of the excited states being probed by the EELS experiments and the electronic structure reconfiguration of the doped material around the single atom dopants. Results directly confirm the possibility of tailoring the plasmonic properties of graphene in the ultraviolet waveband at the atomic scale, a crucial step in the quest for utilizing it’s properties toward the development of plasmonic and optoelectronic devices. The gentle STEM observation conditions can also be used to controllably drive the diffusion of substitutional dopants through single layer graphene, one atomic jump at a time. Atomically precise manipulation with STEM relies on recent advances in instrumentation that have improved the instruments’ stability and their beam positioning abilities. While momentum transfer from highly energetic electrons often leads to atom ejection, interesting dynamics can be induced when the transferable kinetic energies are comparable to bond strengths in the material. For instance, a combined experimental and theoretical study revealed that for Si dopants manipulated in the STEM by 60keV electrons these jumps are not due to impacts on the Si atom, but to sub-threshold impact events on the surrounding C atoms. This approach suggests that STEM could emerge as an alternative method for the direct assembly of nanostructures.

Extending Additive Manufacturing to the Atomic Scale Focus Topic

Room 102B - Session AM+MP+NS-WeA

Atomic Scale Manipulation with SPM

Moderator: Sven Rogge, University of New South Wales, Australia

2:20pm **AM+MP+NS-WeA-1 Advanced Scanning Probe Lithography: Processes, Nanopatterning and Nanoelectronics***, **Ricardo Garcia,*** Inst Ciencia Materiales Madrid, CSIC, Spain **INVITED**

The nanoscale control afforded by scanning probe microscopes has prompted the development of a wide variety of scanning probe-based patterning methods. Some of these methods have demonstrated a high degree of robustness and patterning capabilities that are unmatched by other lithographic techniques. However, the limited throughput of scanning probe lithography has prevented their exploitation in technological applications. Here, we review the fundamentals of scanning probe lithography and its use in materials science and nanotechnology. We introduce several methods, interactions and/or processes such as chemical, mechanical or thermal that enable the tip to modify surfaces. In particular, the presentation is focused on describing the fundamentals and applications of oxidation SPL for nanopatterning and device fabrication of nanoscale field-effect transistors, quantum dots, biosensors and molecular architectures involving a variety of systems from 2D materials to biomolecules; from self-assembled monolayers to silicon.

References

-R. Garcia, A.W. Knoll, E. Riedo, Advanced scanning probe lithography. *Nature Nanotechnology* **9**, 577-587 (2014)

-Y.K. Ryu, R. Garcia, Advanced oxidation scanning probe lithography. *Nanotechnology* **28**, 142003 (2017).

-A.I. Dago *et al.* Chemical and structural analysis of sub-20 nm graphene patterns generated by scanning probe lithography, *Carbon* **129**, 281 (2018).

3:00pm **AM+MP+NS-WeA-3 Integrated Devices made Using Atomically Precise Advanced Manufacturing***, D Ward, D Campbell, M Marshall, T Lu, L Tracy, L Maurer, A Baczweski, **Shashank Misra,*** Sandia National Laboratories

Atomically precise advanced manufacturing (APAM) has enjoyed considerable success in demonstrating high profile physics demonstrations, such as the single atom transistor. However, a considerably broader application space would open up if other transistor elements could be integrated with APAM devices, opening the door to high gain and room temperature operation. However, integration is generally limited by the high temperatures required to prepare pristine silicon substrates for APAM, and by the low temperatures at which phosphorus donors diffuse away once placed into silicon once APAM is complete. Here, we describe progress in integrating metal-dielectric surface gates to achieve high gain, and compensation doping to achieve room temperature operation. The Digital Electronics at the Atomic Limit (DEAL) project is supported by Sandia's Lab Directed Research and Development Program, and was performed in part at the Center for Integrated Nanotechnologies, a U.S. DOE Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

4:20pm **AM+MP+NS-WeA-7 Electrical Transport Properties of Si:P δ-layer Devices***, **Ranjit Kashid**, X Wang, P Namboodiri, J Hagmann,* National Institute of Standards and Technology (NIST)*; S Schmucker,* University of Maryland College Park*; J Wyrick, C Richter, R Silver,* National Institute of Standards and Technology (NIST)

Si:P has been realized as one of the ideal systems for donor-based quantum computation. Site-selective doping of phosphorous atoms at the atomic scale using Scanning Tunneling Microscopy (STM) lithography on the Si(100) 2×1:H surface enables the fabrication of these devices. In the past, our group has demonstrated that degenerately doped & well confined Si:P monolayers can be fabricated using phosphine dosing and low-temperature Molecular Beam Epitaxy (MBE). In addition, a wide range of 1D and 2D nanoscale devices can be fabricated by combining STM lithography and low-temperature MBE. Here, we present magnetotransport and low-frequency 1/f noise measurements on degenerately doped 1D nanowires, 2D Hall Bars, and van der Pauw structures defined using STM lithography. Specifically, we investigate the dephasing mechanism and present a comparative analysis of transport between STM patterned and mesa etched Si:P δ-layer van der Pauw structures to further elucidate the effects of STM patterning on transport properties.

4:40pm **AM+MP+NS-WeA-8 Atomically Precise Tip Positioning for Automated Writing of Atomic-scale Devices***, **James Owen**, E Fuchs, J Randall, J Von Ehr,* Zyvex Labs

Hydrogen depassivation lithography has enabled unprecedented sub-nanometer precision in the positioning of dopant atoms in silicon,[1] advancing the field of silicon quantum electronics. It has also been used for localised atomic layer deposition of Si [2] and TiO_2[3].

In pursuit of our overall vision of Atomically Precise Manufacturing, we are pursuing a number of tactics towards automated fabrication of atomically precise structures. STM lithography vectors are automatically aligned to the surface atomic lattice, and patterns can be input as geometric shapes or arbitrary bitmaps. To improve tip position precision, we have developed real-time creep and hysteresis error correction. Using this, we have previously demonstrated open-loop atomic precision patterning over length scales up to 100 nm. Above this scale, where hysteresis errors are more significant, we are able to reduce the position errors by ~90%.

In parallel with real-time position corrections, we have developed automatic fiducial alignment routines. The tip position can either be aligned to previously-drawn patterns or to deliberate fiducial marks. A large pattern can therefore be stitched together from write fields within which atomic precision can be obtained. Thus, precise patterning can be scaled to large areas.

In the burgeoning field of Quantum Metamaterials[4], large arrays of single dopant atoms are required, with extreme position precision and very high yield. However, the yield of the current thermal process for P limits the yield to 70%[5].

Based on recent work on removal of H from surface PH_2 species[6], we are developing a tip-assisted incorporation process, which prevents the recombination and desorption process. For this application, we need to write single-dimer patterns to adsorb only one PH_3 molecule. For these small patterns, Automated Feedback Controlled Lithography is used, so as to remove exactly the required H atoms from the surface. We are working to improve the detection of the H atom removal, using not only the spike in tunnel current but also the change in the local barrier height [7].

1. M. Fuechsle, et al. *Nat Nano* **7** 242-246 (2012) DOI:: 10.1038/nnano.2012.21
2. J. H. G. Owen et al., J. Vac. Sci. Technol. B **29**, 06F201 (2011).
3. J. B. Ballard, J. H. G. Owen, et al. *J. Vac. Sci. Technol. B*, **32**, 41804 (2014).
4. J. Salfi, et al. *Nat. Commun.*, **7**, 11342, (2016).
5. J. G. Keizer, S. Koelling, P. M. Koenraad, and M. Y. Simmons *ACS Nano***9** 12537-12541 (2015)
6. Q. Liu, Y. Lei, X. Shao, F. Ming, H. Xu, K. Wang, and X. Xiao, *Nanotechnology*, **27**(13), 135704, (2016).
7. F. Tajaddodianfar, S. O. R. Moheimani, J. Owen, and J. N. Randall, *Rev. Sci. Instrum.*, **89**(1), 13701, (2018)

5:00pm **AM+MP+NS-WeA-9 Kilobyte Scale Data Storage through Autonomous Atom Assembly***, S Otte, **David Coffey**,* Delft University of Technology, Netherlands **INVITED**

The ability to manipulate individual atoms by means of scanning tunneling microscopy (STM) opens op opportunities for storage of digital data on the atomic scale. Recent achievements in this direction include data storage based on bits encoded in the charge state, the magnetic state, or the local presence of single atoms or atomic assemblies. However, a key challenge at this stage is the extension of such technologies into large-scale rewritable bit arrays. We demonstrate a digital atomic scale memory of up to 1 kilobyte (8,000 bits) using an array of individual surface vacancies in a chlorine terminated Cu(100) surface. The chlorine vacancies are found to be stable at temperatures up to 77 K. The memory, crafted using scanning tunneling microscopy at low temperature, can be read and re-written automatically by means of atomic scale markers, and offers an areal density of 502 Terabits per square inch, outperforming state-of-the-art hard disk drives by three orders of magnitude.

5:40pm **AM+MP+NS-WeA-11 Extending the Capabilities of STM-based Dopant Device Fabrication***, T Skeren, N Pascher, S Köster,* ***Andreas Fuhrer****,* IBM Research - Zurich, Switzerland **INVITED**

Since the invention of the first bipolar transistor, integrated circuits have evolved to incredibly complex, ultra-scaled devices with on the order of 10^9 transistors per chip. Even if these devices no longer rely on bipolar technology, excellent control of highly doped regions is still a critical factor for device performance. Moreover, single dopant atoms in a silicon crystal or nanoscale silicon transistors are thought to be candidates for spin qubits with a long spin lifetime.

The hydrogen resist lithography technique is capable of preparing atomic scale planar dopant devices. This is enabled by a large difference in chemical reactivity of the bare and hydrogen passivated Si (001): 2x1 surface. Using a scanning tunneling microscope (STM), the hydrogen layer of the H:Si (001) surface is locally desorbed with nanometer precision, exposing areas of reactive Si. When a gaseous dopant precursor such as phosphine or diborane is introduced, the hydrogen layer acts as a resist and the dopants stick only to the desorbed areas. Compared to conventional fabrication methods, hydrogen resist lithography enables degenerate d-doping with sub-nanometer lateral resolution and abrupt doping profiles.

We have extended the hydrogen-resist technique to p-type doping with diborane and present electrical transport measurements on p-type dopant wires and a simple planar pn-junction fabricated by STM patterning.

In addition, we have developed a CMOS compatible device platform for STM-based atomic-scale device fabrication. The scheme uses pre-fabricated samples with electrical contacts and alignment markers and a hydrogen terminated, reconstructed Si:H(001) surface that is protected from the ambient environment by a capping chip.

The sample surface can be used directly for STM-patterning and atomic device fabrication after in-situ removal of this capping chip. After STM device-fabrication the samples are reintegrated into the CMOS workflow by hydrophobic bonding for wafer scale contacting.

Full functionality of this approach is demonstrated with magnetotransport measurements on degenerately doped STM patterned Si:P nanowires up to room temperature, made possible by the use of silicon on insulator substrates.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

SPM – Probing Chemical Reactions at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures***, **Michael F. Crommie,*** University of California at Berkeley Physics Dept. **INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces***, **Christopher Goodwin,*** University of Delaware*; A Maynes,* Virginia Polytechnic Institute and State University*; Z Voras,* University of Delaware*; S Tenney,* Center for Functional Nanomaterials Brookhaven National Laboratory*; T Beebe,* University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure if the resulting films, scanning tunneling microscopy and evaluation of valance band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy***, **Tomasz Michnowicz,*** Max Planck Institute for Solid State Research, Germany, Deutschland*; B Borca,* Max Planck Institute for Solid State Research, Germany*; R Pétuya,* Donostia International Physics Centre, Spain*; M Pristl, R Gutzler, V Schendel, I Pentegov, U Kraft, H Klauk,* Max Planck Institute for Solid State Research, Germany*; P Wahl,* University of St Andrews, UK*; A Arnau,* Donostia International Physics Centre, Spain*; U Schlickum, K Kern,* Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetracenothiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy***, **Giovanni Costantini,*** University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution***, **Seong Heon Kim,*** Samsung Advanced Institute of Technology, Republic of Korea*; S Park, H Jung,* Samsung Advanced Institue of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) particles which are representative LIB cathode materials was studied [1]. After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, Nano Energy 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

Author Index

Bold page numbers indicate presenter

Author Index