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 Dyckoe, Oak Ridge National Laboratory

8:00am **AM+NS+SS-WeM1 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.D. Fowlkes,* Oak Ridge National Laboratory*; P.D. 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-WeM3 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.B. Lewis,* Carl Zeiss Microscopy, LLC*; A. Fernandez-Pacheco, L. Skoric, D. Sanz-Hernandez,* University of Cambridge*; M.G. Stanford, E. Mutunga, P.D. 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.

11:00am **AM+NS+SS-WeM10 Single Atom Scale Manipulation of Matter by Scanning Transmission Electron Microscopy***, **Stephen Jesse**, O. Dyckoe, S.V. 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.

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11:40am **AM+NS+SS-WeM12 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.C. 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*; JA. 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.

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