

MM 35: Nanomaterials: Structure & Properties

Time: Thursday 15:45–18:30

Location: H46

MM 35.1 Thu 15:45 H46

Structural and Electronic Reconstruction of Hexagonal Boron Nitride Interlayers Steps — ●SUBAKTI SUBAKTI^{1,2}, MOHAMMADREZA DAQIQSHIRAZI³, FELIX KERN^{1,2}, DANIEL WOLF¹, THOMAS BRUMME³, BERND BÜCHNER^{1,2}, and AXEL LUBK¹ — ¹Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany — ²Institut für Festkörperphysik, TU Dresden, D-01062 Dresden, Germany — ³Chair of Theoretical Chemistry, Technische Universität Dresden, Bergstrasse 66, 01069 Dresden, Germany

The electrostatic potential of condensed matter provides not only atomic structure, but also the electronic structure that underlies the chemical bonding formation of atoms within one molecule. Off-axis electron holography (EH) technique allows us to probe the volume-averaged electrostatic potential (in crystalline materials over the unit cell) of the specimen with respect to a vacuum reference region. Therefore, a conjunction EH medium and high resolution data analysis and electrostatic potential based ab-initio calculation will be powerful for simultaneous atomic scale reconstruction and imaging. Visible projected potential jump at the edges of two adjacent monolayers hexagonal boron nitride (h-BN) will be addressed here as our data analysis suggest that it could be signature for the increased charge delocalization due to the formation of an additional covalent bond of the 2p orbitals in the rolled-up edge.

MM 35.2 Thu 16:00 H46

Atom Probe Study of self-assembled Monolayers — ●HELENA SOLODENKO, PATRICK STENDER, and GUIDO SCHMITZ — University of Stuttgart, Institute for Materials Science, Heisenbergstr. 3, 70569 Stuttgart

Atom probe tomography is a well-established characterization technique for metals, semiconductors, oxides and minerals. However, measurement of organic matter and biological materials is still challenging. Field evaporation of organic species leads to detection of C_xH_y groups, instead of single atoms. The fragmentation of the molecules possibly depends on the applied electric field strength and the nature of chemical bonding. Self-assembled monolayers (SAMs) represent a suitable model system to study the fundamental questions about field evaporation of such systems, since they represent a well-defined molecular film with a limited number of possible molecular fragments. Furthermore, a chemical bond is formed between substrate surface and the head-group the SAM. By variation of the field strength, we expect to learn more about the field evaporation process and thus about the binding energies of the SAMs. We present measurements of alkane-thiolates on Pt and silanes on ZnO by laser-assisted APT. The backbone evaporates in the form of small hydrocarbon fragments consisting of one to four C atoms, while S evaporates exclusively as single ions. With increasing laser power, a significant trend towards larger fragment sizes is observed. Furthermore, comparison with liquid alkanes and cross linked alkane networks is insightful which demonstrates a continuous transition from evaporation of complete molecules to single atoms.

MM 35.3 Thu 16:15 H46

Tuning the Electronic Properties of Mesocrystals — ●STEFAN MANUEL SCHUPP¹, CHRISTIAN JENEWEIN², BING NI², LUKAS SCHMIDT-MENDE¹, and HELMUT CÖLFEN² — ¹University of Konstanz, Department of Physics, Universitätsstraße 10, 78462 Konstanz, Germany — ²University of Konstanz, Department of Chemistry, Universitätsstraße 10, 78462 Konstanz, Germany

Colloidal crystals consisting of periodically aligned nanocrystalline building blocks, so-called mesocrystals, are promising candidates for nanostructured metamaterials. The high degree of order of the nanoparticles in the crystal results in a well-defined facet-to-facet distance which is determined by the used capping agents. In this work, we were able to grow micrometer-sized platinum nanocube-based mesocrystals with various capping agents and perform electrical measurements on individual crystals with a nanoprobe system. The extracted resistances increase with larger interparticle distances which can be attributed to the predominantly thermally activated tunneling mechanism in these superstructures. However, an additional annealing step leads to a decrease in resistance by seven orders of magnitude due to formed mineral bridges. After this treatment, the electronic

properties are mainly determined by the nanomaterial itself. Finally, we were able to transfer these findings onto multi component superstructures consisting of platinum and iron oxide nanocubes. In these binary mesocrystals the ratio of the nanoparticle types can be varied to tune the electrical conductivity even further while simultaneously allowing to combine properties of both nanomaterials.

MM 35.4 Thu 16:30 H46

Direct Visualization of Ordered Mesoporous Silica Using Atom Probe Tomography — ●KUAN MENG and GUIDO SCHMITZ — University of Stuttgart, Institute for Materials Science, Heisenbergstr. 3, 70569, Stuttgart, Germany

Inspired by enzyme catalytic reaction, heterogeneous catalysis with mesoporous support materials is considered as the fundamental for modern chemical synthesis. However, the synergistic interplay between the catalysts and the pores is still unknown. To realize this, the structure of the mesoporous supports needs characterizing at first. Atom Probe Tomography, due to its subatomic resolution, strong chemical mapping power and direct visualization capability, is becoming a great candidate for mesoporous structure characterization. Yet to unfold its charm, pores must be filled.

In this work, Ordered Mesoporous Silica (OMS) filled with two different polymers, CDEAB and DCPD, was investigated. Firstly, both obtained mass spectra can be interpreted as a plausible combination of signature peaks between silica and polymers. Secondly, the porous network of OMS was visualized using neighboring analysis and the pore size turned out in the mesoporous range. Especially in the case of OMS filled with DCPD, the visualized network appeared to be regularly hexagonal, showing great resemblance with TEM images from similar pore orientations. Last, the obtained data were compared with the result of TAPsim simulations in order to understand the flaws in the visualization and to improve the understanding of the reconstructions.

MM 35.5 Thu 16:45 H46

plastic deformation of nanoporous gold modified with organic layers: a TEM study — ●XIN ZHANG and NADIA MAMEKA — Institute of Materials Mechanics, Helmholtz-Zentrum hereon, 21502 Geesthacht, Germany

As a result of their large specific surface area, strength of high-specific area materials must be sensitive to environment and surface chemistry. This notion is confirmed, e.g., by the enhanced flow stress found in single metal nanowires [1] and metallic networks like nanoporous metals when their surface is modified by adsorbed layers or surface coatings [2]. Yet, experimental studies of microstructural origins of the surface constraints impact on small-scale plasticity is still in its infancy. Here, we examine a defect structure of plastically deformed nanoporous gold (NPG) via ex-situ transmission electron microscopy. We exploit self-assembled monolayers (SAM) to modify a surface of NPG as inspired by a substantial flow stress increase due to SAM adsorption reported in [3]. In bare NPG deformed by rolling, we reveal higher density of twins consistent with [4]. In the deformed NPG with SAM, the formation of twins is strongly suppressed near the surface. Meanwhile, the existence of the organic layer apparently increases the density of twins in NPG. In the contribution, we discuss the TEM observations and link them to the findings from mechanical tests of the SAM-modified NPG. [1] Shin et al, Acta Mat. 166 (2019) 572e586. [2] Wu et al, Mater. Res. Lett. 6 (2018) 508. [3] Mameka et al, ACS Appl. Nano Mater. 1 (2018) 6613. [4] Liu, Weissmüller, Mater. Res. Lett. 9 (2021) 359.

15 min. break

MM 35.6 Thu 17:15 H46

Electrochemical actuation and tunable stiffness of hierarchical nanoporous gold via surface modification — ●OLGA MATTS and NADIA MAMEKA — Helmholtz-Zentrum Hereon, Geesthacht, Germany

Recently developed dealloying strategies towards nanoporous metals with structural hierarchy [1] open up new opportunities for functional behavior of this class of materials. The larger pores at the higher hierarchical level (characterized by diameters around 200 nm) of the hier-

archical nanoporous metals (hc np) can promote fast mass exchange, while nanopores at the lower hierarchy level (below 30 nm) provide a large surface area. To explore the notion we employ electroactive self-assembled monolayers and conductive polymer polypyrrole for surface functionalization of hc np Au and np Au with unimodal pore size. Actuation and Young's modulus behavior of the hybrid materials were then analyzed in situ in a dynamical mechanical analyzer and dilatometer upon potential cycling in aqueous electrolytes. We revealed pronounced variations in the macroscopic length change as well as elastic modulus in response to the voltage-induced redox reactions of the organic films at the np electrodes. In the contribution, we discuss the origin of the observations and compare the functional performance of both types of the hybrids based on np Au.

[1] Shi et al., Science 371, 1026*1033 (2021).

MM 35.7 Thu 17:30 H46

Laser-Ultrasonics Reveals the Complex Mechanics of Nanoporous Silicon — ●MARC THELEN¹, NICOLAS BOCHUD², MANUEL BRINKER¹, CLAIRE PRADA³, and PATRICK HUBER^{1,4,5} — ¹MXP, TUHH, Hamburg, Germany — ²MSME, CNRS UMR 8208, UPEC, Univ Gustave Eiffel, Creteil, France — ³Institut Langevin, ESPCI Paris, Université PSL, CNRS, Paris, France — ⁴CXNS, DESY, Hamburg, Germany — ⁵CHyN, UHH, Hamburg, Germany

Nanoporosity in silicon leads to completely new functionalities of this mainstream semiconductor with numerous discoveries in fields ranging from nanofluidics and biosensorics to drug delivery, energy storage and photonics. Nevertheless, the mechanical properties, critical for a variety of applications, remain difficult to characterise comprehensively. The study presented here aims to address this problem by utilising laser-excited elastic guided waves, detected in dry and liquid-infused porous silicon. Among other things, the experiments reveal that the self-organised formation of 100 billions of parallel nanopores per square centimetre cross section results in an effective stiffness reduction of about 80 %, a nearly isotropic elasticity perpendicular to the pore axes and a higher stiffness along the pore axis, altogether leading to significant deviations from bulk silicon. This thorough assessment of the wafer-scale mechanics of nanoporous silicon and recent breakthroughs in laser ultrasonics therefore open up entirely new frontiers for in-situ, non-contact and non-destructive mechanical characterisation of complex porous material systems [1].

[1] Thelen, M., Bochud, N. et al., Nat Commun., 12, 3597 (2021)

MM 35.8 Thu 17:45 H46

Fabrication and compressive behavior of monolithic nanoporous niobium at macroscale — ●SEYUN SOHN^{1,2}, SHAN SHI^{2,1}, JÜRGEN MARKMANN^{1,2}, and JÖRG WEISSMÜLLER^{2,1} — ¹Institute of Materials Mechanics, Helmholtz-Zentrum hereon, Geesthacht, Germany — ²Institute of Materials Physics and Technology, Hamburg University of Technology, Hamburg, Germany

Studying the mechanical performance of nanoporous (np) metals allows us to understand nanoscale solids as well as to design functional applications. However, the majority of studies have been confined to face-centered cubic noble metals such as gold and palladium due to high electronegativity which facilitates preparation by dealloying. Since the electrochemical or chemical dealloying involves a selective dissolution of less noble constituent(s) in an electrolyte solution, the remaining constituent should be nobler to form a bicontinuous porous structure. Niobium (Nb) on the other hand is less noble than gold, has higher stiffness and lower ductility, and its crystal lattice is body-centered cubic. In this work, np Nb was fabricated out of Ni₇₅Nb₂₅ by liquid metal dealloying; the ligament size could be controlled from 400

nm to more than 1 μm by adjusting dealloying time and temperature. Each sample body is a few mm in size and freestanding, which allows us to perform conventional macro-compression tests to measure the strength and stiffness of the nano-ligament scaffold. Our observations support that the material strength is enhanced with smaller ligaments. More interestingly, our np Nb shows extremely anomalous compliance.

MM 35.9 Thu 18:00 H46

Maximal Anderson Localization and Suppression of Surface Plasmons in Two-Dimensional Random Au Networks

— ●JOHANNES SCHULTZ¹, KARL HIEKEL², PAVEL POTAPOV¹, PAVEL KHAVLYUK², ALEXANDER EYCHMÜLLER², and AXEL LUBK¹ — ¹Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany — ²Chair of Physical Chemistry, TU Dresden, Zellescher Weg 19, 01069 Dresden, Germany

2D random metal networks possess unique electrical and optical properties, such as almost hundred percent optical transparencies and low sheet resistance, which are closely related to their disordered structure and may be exploited in various applications. Here we present a detailed experimental and theoretical investigation of their plasmonic properties, revealing Anderson (disorder-driven) localized surface plasmon (LSP) resonances of large quality factors and spatial localization close to the theoretical maximum. The LSPs typically consist of multiple field hotspots with a well-defined correlation distance. Moreover, they disappear above a geometry-dependent threshold at ca. 1.6 eV in the investigated networks, explaining their large transparencies in the optical spectrum. Electron energy loss spectroscopy in combination with scanning transmission electron microscopy was applied for the experimental studies. Both, the high spatial (≈ 1 nm) and spectral (≈ 50 meV) resolution allows to study the variety of LSP modes in terms of excitation energy and spatial localization. The theoretical study is based on a coupled dipole model, which allows modeling of large plasmonic systems by exploiting Babinet's principle.

MM 35.10 Thu 18:15 H46

Laterally aligned nanowires: Targeted process design and alignment control

— ●JASMIN-CLARA BÜRGER, SEBASTIAN GUTSCH, and MARGIT ZACHARIAS — Laboratory for Nanotechnology, Department of Microsystems Engineering - IMTEK, University of Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany

For sensors, tin oxide nanowires (NWs) have shown superior properties due to their unique geometry, which allows for high sensitivities. NWs are often grown in freestanding mode for which metallization via standard lithography techniques is not applicable. In the production of single NW-based sensors, a multistep process has to be applied and an individual contacting of the NWs by, e.g., e-beam lithography becomes mandatory. Here, the use of planar NWs, i.e., laterally aligned NWs, is of advantage since the removal step from the growth substrate can be skipped and the NWs can be grown at defined positions. Due to their epitaxial contact with the monocrystalline growth substrate, the NWs are self-aligned towards the substrate lattice. However, the parameter space of these NWs is even smaller than for freestanding NWs. Based on finite element simulation and thermodynamic considerations, we developed a model for the growth of laterally aligned NWs.[1,2] The simulations and theory are supported by experimental results. Following, the preparation of longitudinal TEM lamella of individual NWs and AFM measurements allowed us for nanoscopic insight into the NW alignment on the growth substrate.[2]

[1] J.-C. Bürger et al., Beilstein J. Nanotechnol. (2020), 11, 843-853;
[2] J.-C. Bürger et al., Cryst. Growth Des. (2021), 21 (1), 191-199