

Invited Speaker

1197 Quantifying nanoscale diffusion phenomena using in situ TEM

Dr. Peter Schweizer

Oral Presentation

66 Quantification and Control of Mass Transport in different Liquid-Phase Transmission Electron Microscopy Flow Scenarios

Stefan Merkens¹, Giuseppe De Salvo¹, Christopher Tollan¹, Katarzyna Bejtko^{2,3}, Marco Fontana^{2,3}, Angelica Chiodoni², Marek Grzelczak^{4,5}, Andrey Chuvilin^{1,6}

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216 Developing a high-temperature solid state electrochemical lab in the TEM

Mr. Søren Bredmose Simonsen¹, Mr. Zhongtao Ma¹, Mr. Kristian Speranza Møhlhave², Mr. Christodoulos Chatzichristodoulou¹

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316 Panta rhei - tuning the radiation chemistry of silver nitrate solutions via flow in LP-STEM

Mr. Andreas Körner^{1,2}, Dr. Birk Fritsch¹, Dr. Paolo Malgaretti¹, Prof. Jens Harting^{1,2}, Prof. Karl Mayrhofer^{1,2}, Dr. Andreas Hutzler¹

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487 Sensing the Invisible: Ultrathin (UT) Membrane Chip for In-Situ Microscopy

Professor, Director Vinayak David¹

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642 Multiscale study of water condensation on aerosols using in-situ Environmental Scanning and Transmission Electron Microscopies

Dr Eric Ehret¹, Dr Louis-Marie Lebas², Dr Annie Malchère², Dr Joseph Vas³, Dr Francisco Cadete Santos Aires¹, Dr Lucian Roiban², Dr Martial Duchamp³, Prof Karine Masenelli-Varlot¹, Dr Thierry Epicier¹

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682 Shedding light on the birth of hybrid perovskites by In-Situ TEM and Synchrotron X-ray scattering

Dr Charles Sidhoum^{1,2}, Dr Doru Constantin³, Dr Dris Ihiawakrim¹, Dr Marc Lenertz¹, Dr Thomas Bizien⁴, Prof. Clément Sanchez^{2,5}, Prof. Ovidiu Ersen¹

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Poster Presentation

72 In situ plasma studies using a direct current microplasma in a scanning electron microscope

Robin De Meyer^{1,2}, Dr. Lukas Grünwald¹, Dr. Dmitry Chezganov¹, Dr. Andrey Orekhov¹, Prof. Sandra Van Aert¹, Prof. Annemie Bogaerts², Prof. Sara Bals¹, Prof. Jo Verbeeck¹

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138 In Situ Study of Self-Organized Memristive Switching in Neuromorphic Nanoparticle Networks using Complementary SEM Methods

Ole Gronenberg¹, Mrs. Blessing Adejube², Mr. Torben Hemke³, Dr. Niko Carstens³, Mr. Oguz Han Asnaz⁴, Dr. Ulrich Schürmann^{1,6}, Dr. Thomas Strunskus^{2,6}, Dr. Franz Faupel^{2,6}, Dr. Thomas Mussenbrock³, Dr. Jan Benedikt^{4,6}, Dr. Alexander Vahl^{2,5,6}, Dr. Lorenz Kienle^{1,6}

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161 MicroReactor for battery materials synthesis in SEM

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235 Continuous EELS spectrum imaging of nano-droplet crystallization heterogeneity

Ben Miller¹, Cory Czarnik¹

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376 Electrochemistry in LP-EM & Effects Induced by Irradiation of Metal Electrodes

Lucía Morales^{1,2}, Andreas Körner^{1,2}, Dr. Birk Fritsch¹, Dr. Damien Alloyeau³, Justin T. Mulvey⁴, Prof. Joseph P. Patterson⁴, Prof. Dr. Karl J.J. Mayrhofer^{1,2}, Dr. Andreas Hutzler¹

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433 In situ size dynamics and manipulation of nanoparticle interaction under electron beam irradiation

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443 Development of simple image processing for in-situ TEM toward live processing

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475 Electron microscopy and X-ray techniques correlative in situ studies in microfluidic conditions on hybrid perovskites

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499 Transfer of Nanomaterials for in-situ TEM with electrical Currents

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535 Novel polymer thin film fabrication for graphitization studied by in situ transmission electron microscopy

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574 Multiscale characterization of plaster setting using operando multiscale liquid-phase Electron Microscopies

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627 In situ TEM holder for liquid cell research with combined electrochemical and thermal stimuli control

Dr. Yevheniy Pivak¹, Dr. Hongyu Sun¹, Dr. Vasilis Papadimitriou¹, MSc Christian Deen-van-Rossum¹, Dr. Andres Alvarez¹, MSc Merijn Pen¹, Dr. Joseph Patterson², Dr. Hugo Perez¹

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811 Towards customized in situ TEM Chips for “device-like” geometries

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1018 Metal-Organic Chemical Vapor Deposition in a Transmission Electron Microscope

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1162 In-situ cryo-biasing heating TEM sample holder with full-range temperature control from -170°C up to >1000°C

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1197

Quantifying nanoscale diffusion phenomena using in situ TEM

Dr. Peter Schweizer

IM-07, Lecture Theater 2, august 26, 2024, 10:30 - 12:30

Quantification and Control of Mass Transport in different Liquid-Phase Transmission Electron Microscopy Flow Scenarios

Stefan Merkens¹, Giuseppe De Salvo¹, Christopher Tollan¹, Katarzyna Bejtka^{2,3}, Marco Fontana^{2,3}, Angelica Chiodoni², Marek Grzelczak^{4,5}, Andrey Chuvilin^{1,6}

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IM-07, Lecture Theater 2, august 26, 2024, 10:30 - 12:30

Background

Liquid-phase transmission electron microscopy (LP-TEM) is an emerging experimental technique which permits the monitoring of processes in liquid samples with nanometer-scale resolution. Over recent years, LP-TEM setups have evolved into sophisticated model reactors for the study of physico-, bio- & electro-chemical processes propelled by the integration of various stimuli such as temperature, electric bias, and reaction media composition. In particular, microfluidic systems have inspired numerous expectations among the community, most notably the control of supply of reagents to and/or reliable removal of unwanted (radiolytic) species from the imaging region. However, the evolution of LP-TEM into a quantitative imaging technique remains limited by several issues, most of which are related to poor calibration of mass transport dynamics in the complex LP-TEM flow channel geometries.[1] Here, we will discuss fundamental aspects of mass transport in LP-TEM flow experiments.

Methods

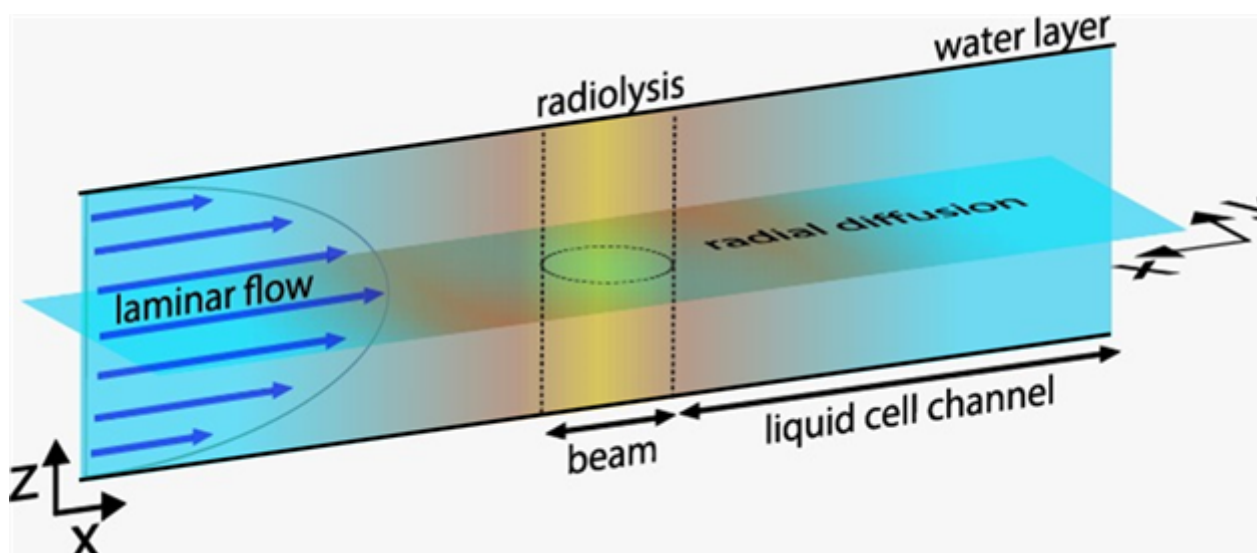
A general approach combining experimental and theoretic methods for the calibration of mass transport in LP-TEM flow systems will be described.[2] The experimental part relies on image contrast variation achieved by flowing a contrast agent. The theoretic part relies on finite element modelling of relevant physics, i.e. convective and diffusive transport, in realistic 3D channel geometries. Both aspects will further be implemented in a rapid prototyping procedure for the fabrication of novel LP-TEM flow reactors: a virtual prototyping step that relies on an experimentally validated model is combined with a physical prototyping step that uses microfabrication routines (lithography and wet-etching). In addition, to study the impact of the established mass transport mechanisms on beam-induced chemistry, the finite element model is further extended by reaction kinetics of radiolysis.

Results & Discussion

A comprehensive understanding of mass transport phenomena in LP-TEM flow scenarios will be provided. First, the bimodal approach is applied to understand the hydrodynamic properties of different LP-TEM flow reactor geometries. In particular, crucial geometric features of the flow channels are identified that result in either convection or diffusion being the dominant transport mechanism.[2] Second, the effect of convective transport on radiolytic reaction networks will be investigated.[3] In contrast to established assumptions, only molecular radiolytic species can be rinsed effectively. In consequence, the concentration of highly reactive species (e.g. H* and e-) follow non-linear trends and increase with increasing flow velocity. The implications of these findings for flow-based scavenging strategies will be highlighted. Thereupon, novel LP-TEM flow setups with diffusion-optimized mass transport properties, which exceed previous constraints by ~2 orders of

magnitude, will be presented.[4] Finally, the benefits of the novel setups are demonstrated through different application examples from the field of materials research and electrochemistry.[5]

We anticipate that the knowledge provided will enable better planning of in situ & in-operando experiments and support more reliable interpretation of results. The rational design of flow reactors will enhance correlatability to ex situ experiments and open new fields of LP-TEM research.



Keywords:

Liquid-Phase TEM, microfluidics, in-situ experiments

Reference:

- [1] Zheng, MRS Bulletin, 2021, 46, 443-450.
- [2] Merkens et al., Ultramicroscopy, 2023, 245, 113654.
- [3] Merkens, De Salvo et al., Nano Express 2023, 3, 4, 045006.
- [4] Merkens et al., Nature Communications, accepted.
- [5] Bejkta, Fontana et al., Nature Communications, in revision (preprint: <https://www.researchsquare.com/article/rs-3660145/v1>)

216

Developing a high-temperature solid state electrochemical lab in the TEM

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IM-07, Lecture Theater 2, august 26, 2024, 10:30 - 12:30

Background incl. aims

Conducting both electrochemical and structural/compositional analysis simultaneously and on a nanoscale level enables a direct correlation between electrochemical performance and the material's properties, tracking their changes over time and different operational conditions¹. The aim of the presented work is to establish a solid method that combines high-temperature solid state electrochemical analysis with (S)TEM^{2,3}. Such a method is crucial for advancing solid oxide electrolysis and fuel cells (SOEC/SOFC) and can be relevant to other solid-state electrochemical technologies such as solid-state batteries and thermoelectric devices.

Methods

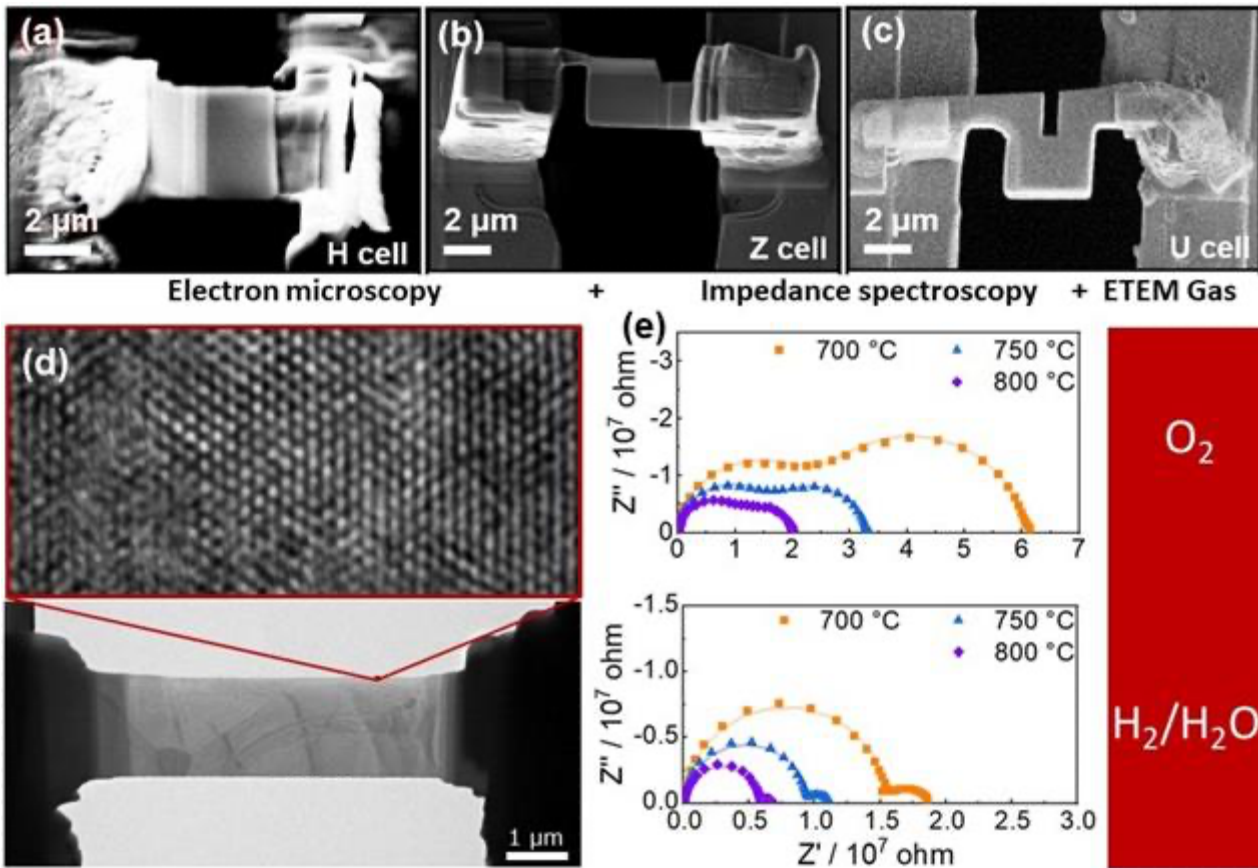
A method development is presented in which MEMS chip-based heating-biasing TEM holders are combined with environmental TEM (ETEM) and a potentiostat for electrochemical impedance spectroscopy (EIS). Various preparation methods and TEM sample geometries are included, such as model solid oxide cells prepared by pulsed laser deposition (PLD), along with an advanced FIB-SEM sample preparation procedure. Operando high-temperature electrochemical (S)TEM experiments are conducted.

Results

The feasibility of conducting electrochemical cell tests in the (S)TEM is demonstrated, including reliable EIS measurements of full solid oxide cells at temperatures up to 800 °C in gases such as O₂ and H₂/H₂O and with applied electrical polarization^{1,2}. The presentation will discuss challenges and necessary requirements for performing such experiments². Examples of EIS analysis in the TEM will be presented^{1,2}. Additionally, results from experiments are presented where polarization-induced degradation at an electrode-electrolyte interface in an SOEC was indicated by EIS analysis and confirmed by electrochemical operando STEM observation.

Acknowledgements

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Keywords:

Operando (S)TEM, electrochemistry, SOEC, SOFC

Reference:

1. Z. Ma, et al., *Small Methods* 7 (2023) 2201713
2. Z. Ma, et al., *Small Methods* (2024) 2301356
3. S.B. Simonsen, et al., *Microsc. Res. Tech.* 86 (2023) 1003-1011

316

Panta rhei - tuning the radiation chemistry of silver nitrate solutions via flow in LP-STEM

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IM-07, Lecture Theater 2, august 26, 2024, 10:30 - 12:30

Background incl. aims

Operando liquid phase electron microscopy (LP-EM) has revolutionized the insights in chemical reactions. Yet, electron irradiation of liquid phases always comes at the cost of radiolysis. Recent advances in simulation allow to estimate the chemical environment and show that the results are drastically altered for different, diluted aqueous systems[1]. With the new generation of liquid cells however, active flow is feasible experimentally to allow a dynamic exchange of the solution.[2] This demands to systematically access these effects. Recently, flow simulations on irradiation of pure water indicate that the flow reduces the local concentration of some, especially long-lived species. Their lack in turn increases the concentration of short-lived reactive species within the irradiated volume.[3] However, experimental validation is pending - a prerequisite to a mature application of LP-EM to more applied systems.

Recent attention has been drawn to silver nanoparticles for CO₂ upconversion. To facilitate such studies in in LP-EM, the radiation chemistry of such systems must be well understood. While the radiation chemistry of AgNO₃ was estimated in TEM, STEM, and under heatin[4] , the impact of direct flow on beam-induced Ag nanoparticle evolution remains an unknown parameter.

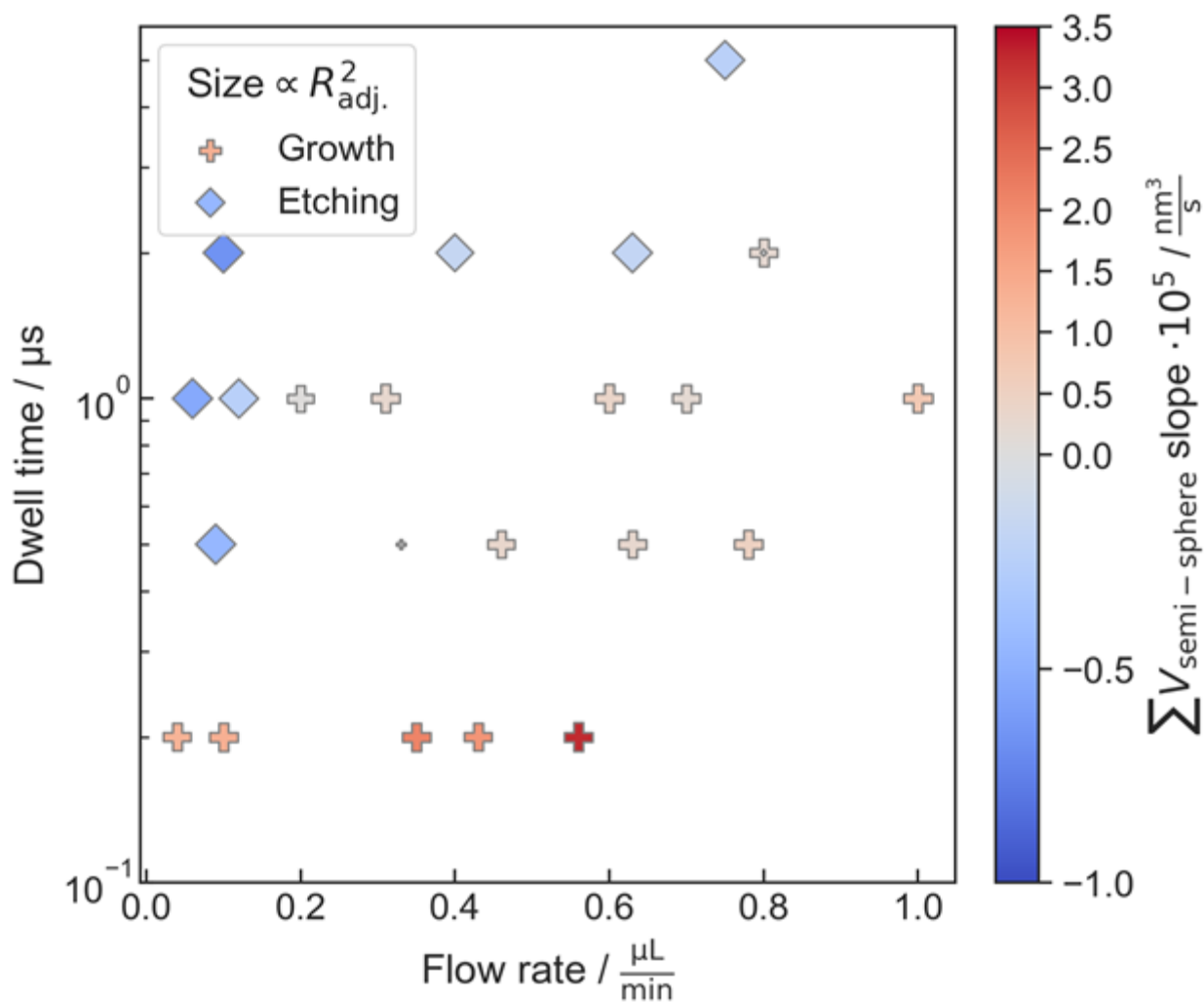
Methods

To overcome this knowledge gap, we provide systematic experiments using a DENSolutions Stream system and a Thermo Fisher Scientific Talos F200i at 200 kV in STEM mode operated with a beam current of 22 pA. By using AgNO₃ as probe solution, we systematically vary flow velocity and dwell time to characterize growth and etching kinetics.

Results

Our findings show that radiolytically-grown Ag nanoparticle behavior ranges from fast growth to dissolution, suggesting a change between reductive and oxidative regime. This is achieved by a change of either flow rate or dwell time, which allowed to empirically map the parameter space. Preliminary results are shown in Figure 1: Growth rate analysis of silver particles (colorbar) for varying dwell times of the scanning electron beam (y-axis) and flow rates(x-axis).

Supporting to the experimental analysis we provide further advances to the automated radiation chemistry tool AuRaCh[5] including interrupted (scanning) irradiation and flow. These findings will provide further insight into the chemistry observed in flowed liquid-phase experiments.

**Keywords:**

LP-EM, silver nanoparticles, flow velocity

Reference:

- [1] Fritsch, Körner (shared) et al., 2023, J. Phys. Chem. Lett. 14, 20
- [2] Beker et al., 2020, Nanoscale 12, 22192-22201
- [3] Merckens et al., 2022, Nano Ex. 3, 045006
- [4] Lee et al., 2023, ACS Nano 17, 6
- [5] Fritsch et al., 2022, Adv. Sci. 9, 2202803

487

Sensing the Invisible: Ultrathin (UT) Membrane Chip for In-Situ Microscopy

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IM-07, Lecture Theater 2, August 26, 2024, 10:30 - 12:30

Background incl. aims

Operando or in-situ S/TEM methods utilizing amorphous silicon nitride (SiN_x) membrane encapsulated chips to confine fluids for electron microscopy have become popular in recent decades. A great number of prior innovators have shown this to be an effective approach for probing fluid-surface/nanostructure interactions and related phenomena. Such “closed-cell” platform has many practical and technological advantages over the differential pumping environmental TEM (ETEM). Unfortunately, however, conventional fluid-cells suffer from additional and significant electron scattering from the top and the bottom membranes, which are typically 30-50nm thick to maintain integrity/stability during the operation. Thus, the total thickness of >60-100 nm of the encapsulating membranes imposes many adverse effects on the post electron optics, such as increased chromatic aberrations. This naturally results in significant degeneration of signal quality and loss of spatiotemporal resolution, diffuse interference in the electron diffraction, and plasmon-dominated electron energy loss spectra (EELS).

Methods

We have recently reported development of a robust, functional and scalable backing support strategy to enable the thinnest possible (<10 nm) SiN_x gas encapsulation material [1, 2]. Inspired by the natural honeycomb geometry, our novel design provides for hexagonal backbone that can neatly anchor ultrathin (~<10 nm) SiN_x membrane with excellent stability and consistent performance. Unlike graphene-based encapsulations, stability under the electron beam is comparable to a 50 nm SiN_x membrane, which is sufficient for most high-resolution S/TEM applications on non-electron sensitive materials.

Results

We show that our UT chip increases contrast of typical nanoparticles at 1 atm Ar gas by ~70 % and the accessible information limit is enhanced by >130 % compared to the conventional encapsulation. More importantly, the t/λ_i is reduced from nominally ~1.0 to 0.3 using a 1 Atm gas cell. This greatly enhances spectral visibility and significantly improved S/N for EELS excitations. Thus, spatiotemporal detection of gas species, down to ~nanometer scale is now being routinely achieved.

Conclusions

The presentation will cover the design and implementation of UT membrane fluid-cell for in-situ gas-solid interactions. It will also argue that combining monochromatic source with UT membrane may open new opportunities for molecular-scale understanding of dynamic fluid-surface phenomena. [3]

Keywords:

Ultrathin (UT) membrane, in-situ microscopy

Reference:

References: [1] K Koo, SM Ribet, C Zhang, PJM Smeets, Rd Reis, X Hu, and VP Dravid, Nano Lett 22 (2022), p. 4137. doi: 10.1021/acs.nanolett.2c00893; [2] VP Dravid, X Hu, and K Koo, US Provisional Patent, No. 63413097 (2022); Science Advances, 2024: DOI: 10.1126/sciadv.adj6417

[3] Acknowledgement: This work is made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the SHyNE Resource (NSF ECCS-2025633), the IIN, and Northwestern's MRSEC program (NSF DMR-1720139). Parts of the research are also supported by US DOE (Hydrogen EFRC), AFOSR (MURI) and NSF-DMR.

642

Multiscale study of water condensation on aerosols using in-situ Environmental Scanning and Transmission Electron Microscopies

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IM-07, Lecture Theater 2, august 26, 2024, 10:30 - 12:30

Background incl. aims

Predicting cloud formation and the arrival of precipitation has always been a hot topic in meteorology. With global warming and the many ongoing drought events, this has become a major issue. Environmental scanning and transmission electron microscopy (respectively ESEM and ETEM) can provide valuable information to understand how clouds are formed by condensation of water on submicronic aerosol particles. Indeed, Environmental Electron Microscopy allows following the structural changes during the condensation of water droplets, while controlling the relative humidity, from the dry state up to fully hydrated conditions.

Methods

Sodium chloride particles are used as model marine aerosols. The deliquescence of crystals in the size range 100 nm – 1 µm is studied in ESEM (QuattroS from TFS) equipped with either a commercial Peltier stage (SE imaging) or a home-made tomographic stage (STEM imaging in both BF and DF modes) [1]. The deliquescence of smaller crystals is studied in ETEM (Titan ETEM from FEI/TFS) using either a commercial cryo-holder from Gatan/Ametek or a home-made system based on a Peltier micro-cooler [2]. More realistic aerosols, such as (non-hygroscopic) Arizona dust decorated with (hygroscopic) sodium chloride, are then studied.

Results

The evolution of the crystal facets and corners as a function of relative humidity is studied in ESEM in the SE mode, and is compared with the literature [3]. The measurement of the relative humidity allows a calibration of the other microscopy set-ups. Interestingly, oscillating behaviors at the beginning of deliquescence could be reproduced and followed in real time in STEM and TEM on smaller crystals (see Figure 1). They were found to match 2D simulations based on local fluctuations of the solute content. The distribution of sodium chloride during hydration/dehydration cycles is also analyzed.

Electron tomography is also carried out at multi-scale, in ESEM and ETEM on hydrated samples and quantitative data can be extracted: crystal shape and size as well as water droplet shape, and the aggregate shape and compound distribution in the case of salted Arizona dust.

Conclusion

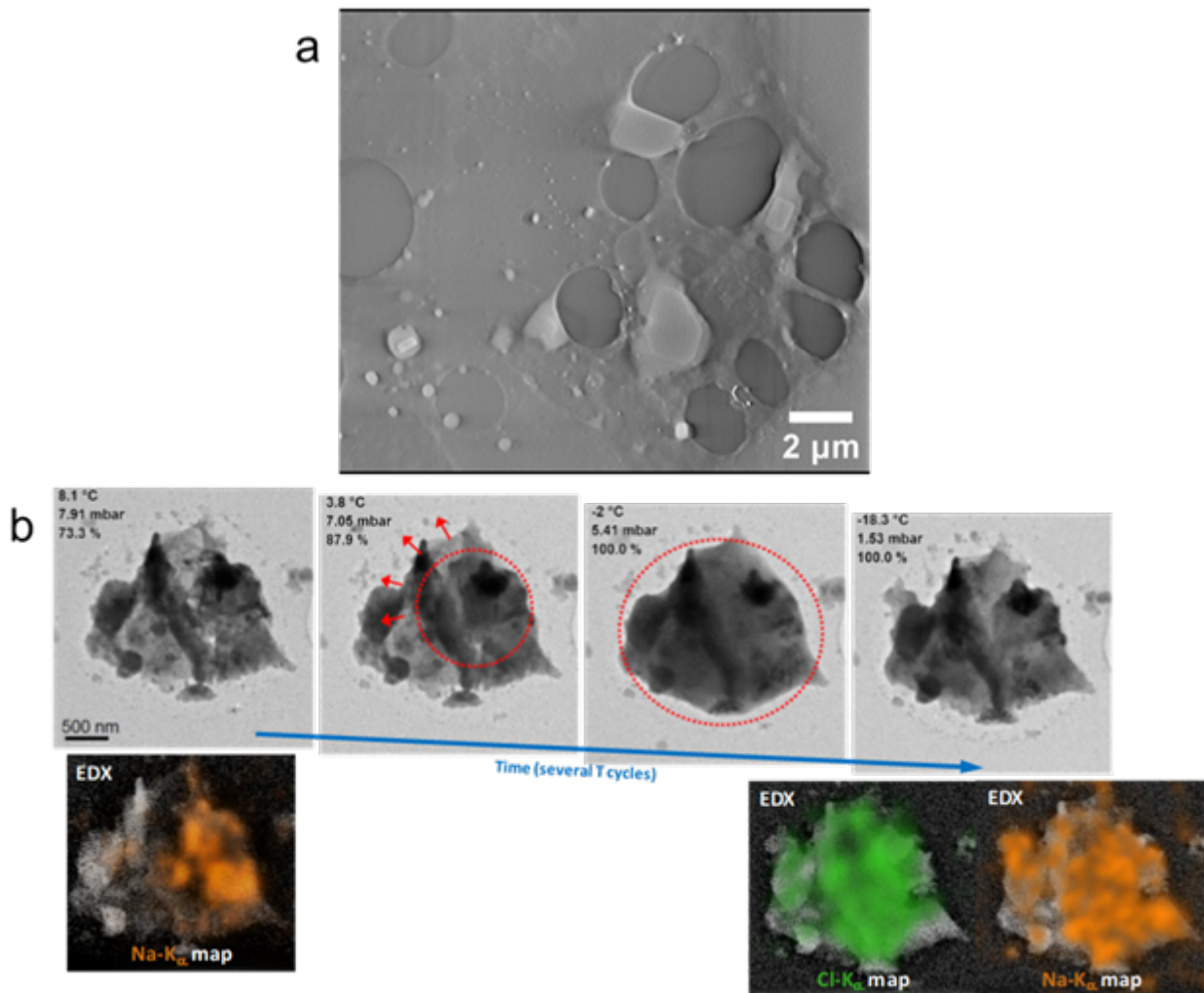
The multi-scale approach combining ESEM and ETEM enable the analysis of salt particles not only in 2D, but also in 3D, for different values of relative humidity. As irradiation damage can have large influence on the observed behavior and kinetics, the electron dose received by the sample is quantified and its effects discussed.

Acknowledgements

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Figure caption

water condensation on aerosols. (a) XY slice of a tomogram obtained in ESEM, showing NaCl crystals within water droplets. (b) Hygroscopic behavior of realistic aerosol (mixed phase Arizona dust and NaCl) with spatial localization and chemical identification of soluble phases during hydration (several T cycles).



Keywords:

ETEM, ESEM, in-situ, liquid

Reference:

- [1] Xiao, J. et al., *Micron*, 117 (2019), 60.
- [2] Vas, J. et al., *Microsc. Microanal.*, 28, S1 (2022), 818.
- [3] Langlet, M. et al., *Chemical Engineering Science* 86 (2013) 78.

682

Shedding light on the birth of hybrid perovskites by In-Situ TEM and Synchrotron X-ray scattering

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IM-07, Lecture Theater 2, august 26, 2024, 10:30 - 12:30

Background

Organic-inorganic halide perovskites (OIHPs) have emerged as promising candidates for a broad range of optoelectronic devices thanks to their unique physical properties¹. In the current framework of energy transition, OIHPs have demonstrated great potential in the photovoltaic field with the development of OIHPs-based solar cell reaching, in 2022, a power conversion efficiency of 25.6%² similar to its silicon-based analog. Methylammonium lead iodide (MAPI) has been the most commonly studied LHPs due to its very promising optoelectronic properties. One of the main explored pathways for obtaining MAPI perovskite is the Ligand-Assisted Reprecipitation (LARP) approach³; however, this method is not totally understood from a phenomenological point of view. Especially, the use of DMF as a polar solvent for the preparation of the precursor mixture leads to the formation of intermediate DMF-solvated phases⁴ before the obtention, by annealing, of the final MAPI phase.

While a large amount of the community is focused on the OIHPs' physical properties with the aim of its application in photovoltaic, very less tackles this subject with an in-situ approach for the study of its growth processes. Thus, we decided to adopt this specific research angle to provides a better understanding of the LARP approach for synthesizing hybrid perovskites.

Methods

In one of our study⁵, we took advantage of the development of microchip-based systems which enabled to study dynamic phenomena in their native environment, e.g. gas or liquid, directly in the TEM vacuum column. By replicating the LARP synthesis protocol in a Liquid-Phase TEM (LPTEM) cell (Figure 1.A), we were able to dynamically track the growth in solution of an intermediate DMF-solvated phase during the LARP process. These observations were correlated with synchrotron-based X-Ray scattering measurements performed on the SWING beamline of the SOLEIL synchrotron. The second part of the study is dedicated to the study of the transition by annealing in air from the intermediate phase toward the final optoelectronically interesting MAPI perovskite material. For this purpose, we have carried out annealing at 80°C in a Gas-Phase TEM (GPTEM) cell using a similar microchip system. We correlated the TEM observations with Temperature-resolved X-Ray diffraction using a chamber dedicated to temperature measurements.

Results

First, we monitored the nucleation and the growth processes of a DMF-solvated-intermediate phase by directly visualizing the reaction medium using LPTEM (Figure 1. B-F). The LPTEM images revealed the formation of roughly spherical objects (Figure 1. C-D) in the early stages of the process transitioning to elongated ribbon-like morphology particles (Figure 1. E-F) after a few seconds, through a crystallization process. These local observations, in direct space, were correlated with more global information brought by synchrotron-based X-ray scattering measurements (Figure 1. G and H). With excellent time consistency with LPTEM imaging (Figure 1. B-F), the X-ray scattering measurements enabled us to identify similar morphology and confirm the local observations from

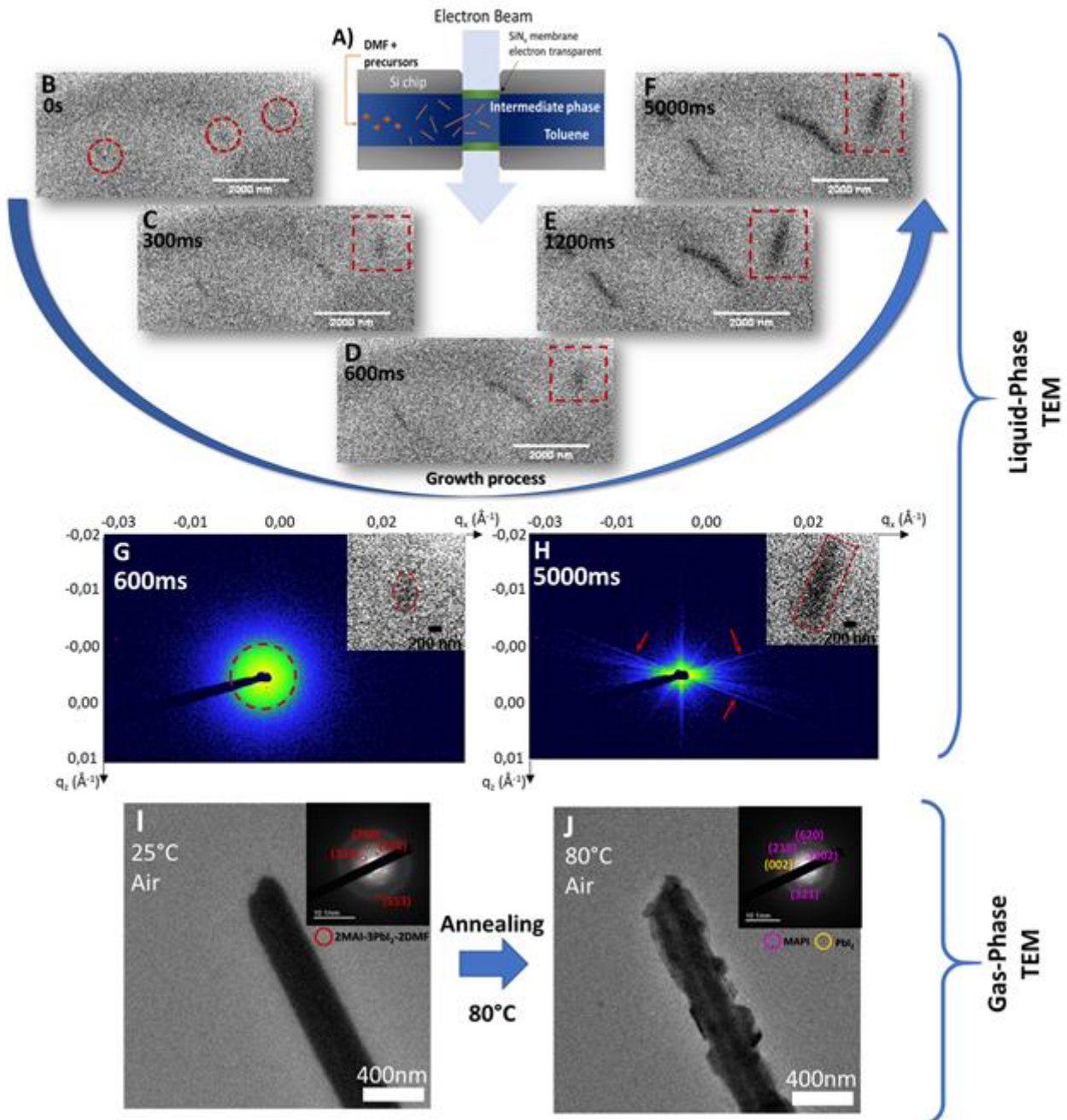
LPTEM. This combined analysis, conducted in real-time and in representative conditions, allowed us to decipher the structural evolution of the emerging phases.

Secondly, we tracked in-situ the transition, occurring in air by annealing at 80°C, of the as-obtained intermediate phase towards the MAPI perovskite, using a combination of GPTEM, in image and diffraction modes (Figure 1. I and J), and temperature-resolved X-Ray diffraction associated with Rietveld refinement. We provided direct and unprecedented evidence of the fragmentation of the crystals, occurring simultaneously with the structural transformation between the intermediate and final phases. While GPTEM evidenced the fragmentation of the ribbon-like crystals into platelets, the Rietveld refinement explained this morphological transition based on a crystalline structure that already exhibited a preferential orientation towards (hk0) and (0k0) family planes.

Conclusion

We have, for the first time, directly visualized the growth of an intermediate phase of hybrid perovskites in liquid media during LARP synthesis using TEM. We show that combining LPTEM observations with synchrotron X-Ray scattering measurements is particularly effective for investigating such phenomena across various scales. Additionally, we investigate the transition of this intermediate phase through annealing and demonstrate how a correlative approach, combining TEM in Gas-Phase and X-Ray measurements, provides new insights into the mechanisms underlying structural changes during crystalline transitions.

Our approach, which required the challenging development of new correlative methods, underscores the significant value of in-situ correlative studies for enhancing our understanding of the synthesis of emerging hybrid materials. There remains a gap in understanding the growth mechanism of these materials in solution and we firmly believe that in-situ TEM-based correlative studies can contribute significantly to addressing these shortcomings.



Keywords:

Hybrid perovskite, In-Situ TEM, Correlative

Reference:

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In situ plasma studies using a direct current microplasma in a scanning electron microscope

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Poster Group 1

Background incl. aims:

Plasmas, sometimes called the fourth state of matter and defined as an ionized gas, have applications in a variety of fields, including biomedicine, materials science, and gas conversion. A typical example of plasma technology is their use in the semiconductor industry, where they fulfill a critical role in the etching process of silicon wafers when fabricating nano-scale components that make up computer chips [1]. At the same time, plasmas are heavily researched to gain further fundamental insights, and to develop novel technologies and applications. These research areas include plasma catalysis, gas conversion, nanomaterial synthesis, and biological treatments [2].

Many of the relevant plasma processes take place at a microscopic scale. However, current diagnostics (e.g., optical techniques) are often limited to global measurements, naturally averaging out microscopic effects. Micro-scale investigations of plasma-treated materials are typically limited to ex situ studies, where post-mortem analyses are performed on samples after plasma treatment [3]. This limits the temporal resolution of current studies, while also exposing the sample to ambient conditions during the transfer from the plasma device to the diagnostic equipment.

Therefore, we aimed to develop a setup that enables the formation of a plasma inside a scanning electron microscope (SEM). Specifically, we sought to achieve true in situ SEM imaging during plasma operation and to investigate the effect of plasma on materials at high spatial and temporal resolution, while preserving the original state of the plasma-treated sample.

Methods:

We modified an environmental SEM to integrate the instrumentation for generating and monitoring a plasma within the chamber [4]. A custom flange was designed to provide a passthrough for electronics and gas supply. The gas supply is connected to a steel tube with a small orifice, which brings the gas close to the sample, and they are both placed in the field of view of the SEM. The sample is grounded, while the nozzle is connected to a DC-DC converter placed inside the chamber which is powered by a DC power supply outside of the microscope. This way, plasmas in a variety of gases were generated by supplying the nozzle with a voltage up to 2 kV. The current flowing through the sample to the ground was measured using a shunt resistor, enabling real-time monitoring of the plasma discharge. While the plasma was on, the SEM could be used in its normal high-vacuum operating mode.

The in situ setup was tested for a range of plasma and imaging conditions. Different discharge gases were used to generate the plasma, including N₂, CO₂, and an O₂/Ar mixture. Flow rates were varied between 2.5 and 7.5 sccm, which was monitored by a mass flow meter outside of the microscope. Further, the distance between the nozzle and the sample could be varied, typically between 75 and 150 μm. This setup offers high flexibility, though a plasma discharge was not possible for all conditions (e.g., large gap distance and low flow rate) at our maximum applied voltage of 2 kV. True in situ imaging was possible with both the secondary electron and backscattered electron mode of the Everhart-Thornley detector, while EDX measurements were performed between plasma treatments.

Results:

To characterize the plasma discharge, we acquired the voltage-current characteristics, where the plasma current was monitored while varying the applied voltage. These data were obtained for a number of gap distances and gas flow rates. These characteristics all exhibit a rising slope and the positions of the curves for varying conditions are indicative of a so-called obstructed abnormal glow discharge. This implies that a discharge should be sustainable at even lower voltages, if the gas density could be increased.

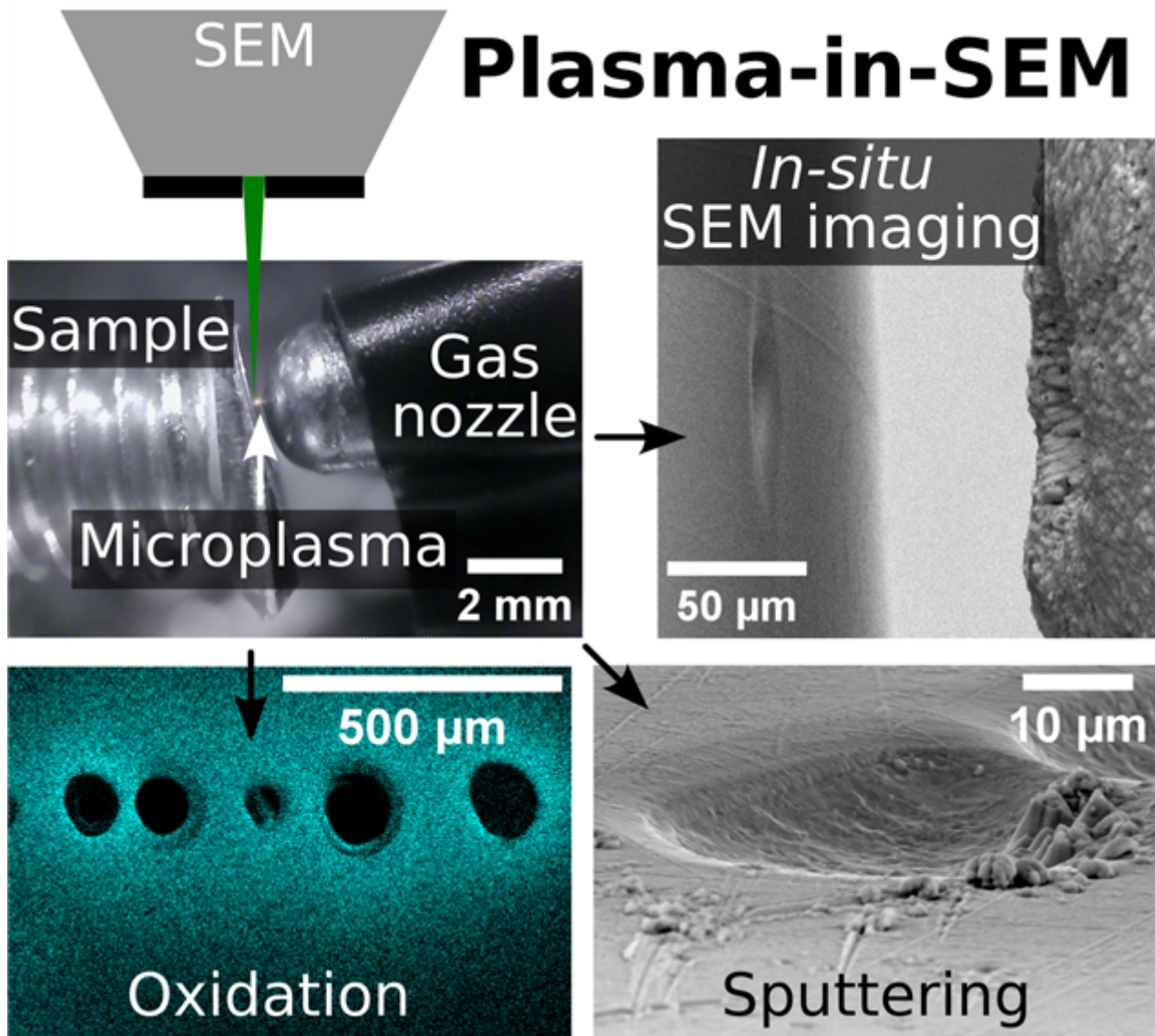
Next, we investigated how the plasma operation affected SEM imaging, showing that true in situ SEM imaging was possible during the plasma discharge. While the electron beam is deflected by the electric field needed to sustain the plasma, the presented setup is sufficiently stable to obtain high-quality SEM images. The deformation of the images by the deflected electron beam must be considered for quantitative image analysis, but regardless the images are suited for qualitative studies. In a proof-of-concept example, a video was captured where the sputtering of the sample could be monitored in real-time. The homogeneous sputtering of the sample also yielded microscopic conical structures, formed out of spherical particles or impurities that were present on the sample surface.

To further explore the SEM-plasma synergy, we employed elemental mapping to study the composition of the sample and how it is affected by various plasmas. Apart from the physical effects of the plasma (i.e., sputtering), chemical reactions were also observed. We showed that oxygen-containing plasmas, e.g., CO₂, can oxidize the Cu sample outside of the sputtered area. For the latter, the sputtering effect was dominant and exposed the pristine Cu below the surface.

Finally, we explored the effect of the voltage polarity on the plasma properties, since a negatively biased electrode accelerates the positive ions to the nozzle rather than to the sample. This yielded sputtering of the nozzle instead of the sample and subsequent redeposition of nozzle material on the sample. At the same time, the sputtering of the sample was strongly limited while the oxidation in a CO₂ plasma could be observed for a broad region.

Conclusions:

This work presents a dedicated setup to generate a plasma inside a scanning electron microscope. The setup enables true in situ SEM imaging, where electron-based images can be acquired while treating the sample with a plasma. The interaction of the plasma and the sample was studied by real-time imaging, where a pit being formed in the sample sheds light on the sputtering behavior of the setup. Moreover, microscopic conical structures were formed by bombarding spherical particles or impurities with ions. Finally, chemical effects of the plasma were observed, where a CO₂ plasma was able to oxidize the Cu sample. This setup is a stepping stone for future research, both in the direction of materials science and toward more advanced plasma diagnostics.



Keywords:

SEM, Plasma, Sputtering, In-situ SEM

Reference:

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In Situ Study of Self-Organized Memristive Switching in Neuromorphic Nanoparticle Networks using Complementary SEM Methods

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Poster Group 1

Background incl. aims

Self-organized nanoparticle networks (NPNs) poised at the percolation threshold are promising for bio-inspired information processing. These networks show non-linear responses, high dimensionality and avalanche dynamics similar to those observed in the brain. The objective of this study is the imaging of the current path through the NPN to study the distributed memristive switching events.

Methods

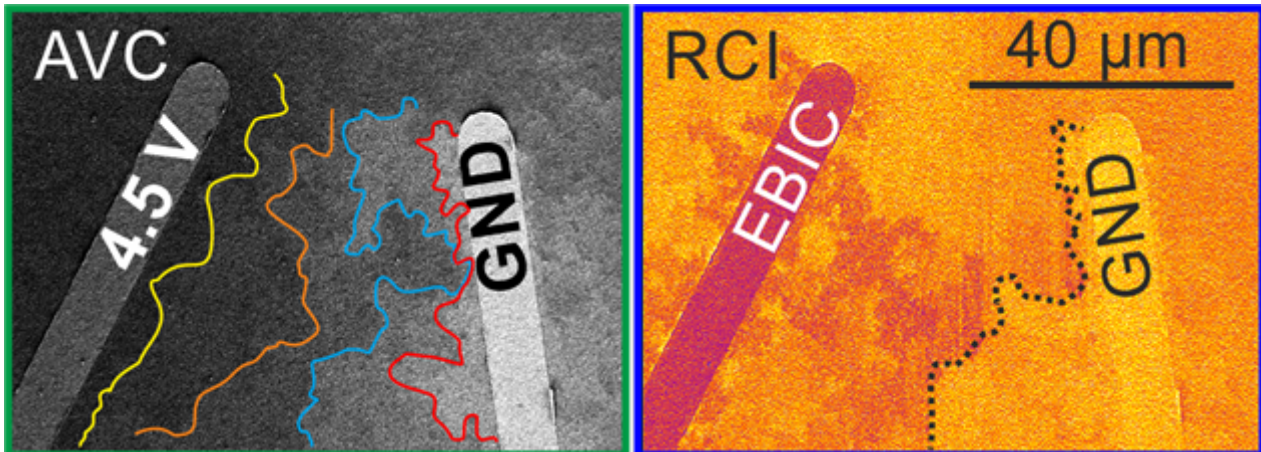
The neuromorphic NPN was fabricated in two steps. First, an insulating base-layer, consisting of Ag NPs with a CxOyHz shell, was deposited on pre-structured Pt electrodes on a Si chip with 1 μm thermal oxide. In a second deposition step, pure Ag NPs were deposited under continuous conductance monitoring until the percolation threshold was reached. The avalanche dynamics of the NPN with features of criticality were analyzed ex situ. Ultimately, this NPN was analyzed in the SEM (FEI Helios Nanolab 600 SEM/FIB with a field emission gun operated at 3 kV) with 2 complementary methods. First, during in operando biasing a changing active voltage contrast (AVC) was observed. Second, resistive contrast imaging (RCI) revealed directly the current path after biasing steps. For these experiments, Pt electrodes below the NPN were electrically connected in situ by micromanipulators with tungsten needles to an EBIC amplifier from Kleindiek company. To gain a better understanding of the current response of NPNs, we corroborate the experimental results with kinetic Monte-Carlo simulations.

Results

After biasing, RCI was used to observe directly the current path (see graphic) revealing changes in the connectivity after successive biasing steps, while the overall morphology of NP groups persisted. AVC revealed a step-like potential distribution (see graphic) that changed during static biasing. Simulations indicated that nano-gaps between NP groups lead to the step-like potential distribution that varies due to switching events.

Conclusion

Current path imaging using AVC and RCI indicates that the current path changes steadily during biasing due to the construction and deconstruction of memristive filaments in nano-gaps between NP groups. The changing position of the nano-gaps is highlighted by strong resistive contrast. Thus, we correlated the avalanche dynamics of the NPN with spatio-temporally distributed resistive switching events within the network with the complementary combination of AVC and RCI.



Keywords:

Resistive-Contrast-Imaging, Active-Voltage-Contrast, Neuromorphic, Memristor, Self-Organization

Reference:

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161

MicroReactor for battery materials synthesis in SEM

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Poster Group 1

Background incl. aims

In-situ SEM can help with understanding and optimization of processes forming (nano-)materials usable in electronic devices and energy storage systems. The high-temperature synthesis of these materials often happens in reactive, explosive, or harmful environments.

This study aimed to prove the functionality of the MicroReactor device for in situ SEM imaging during experiments requiring reactive gases (such as pure hydrogen or hydrogen sulfide) that result in the synthesis of the currently used and possible future battery materials.

Methods

MicroReactor device [1] equipped with a MEMS heating & biasing chip [2] was used in Helios G4 UX and Scios DualBeam systems. The MicroReactor's low-volume reaction chamber, coupled with a retractable lid enabling work with reactive gases during SEM operation and open access for sample preparation by FIB, assures improved process cleanliness and safety compared to an environmental SEM. In-lens detectors of the SEM column as well as STEM or 4D STEM detectors placed below the transparent MEMS chip can monitor changes in the processed sample. Real-time gas analysis of reaction products is possible on the outlet line connected to the reaction volume. After gas-assisted processing, EDS and EBSD analyses can follow while the sample remains heated up to 1200°C. In the latest design, the MicroReactor sample holder can be transferred in argon between a glove box and a FIB-SEM chamber.

Results

Three novel applications of MicroReactor will be presented.

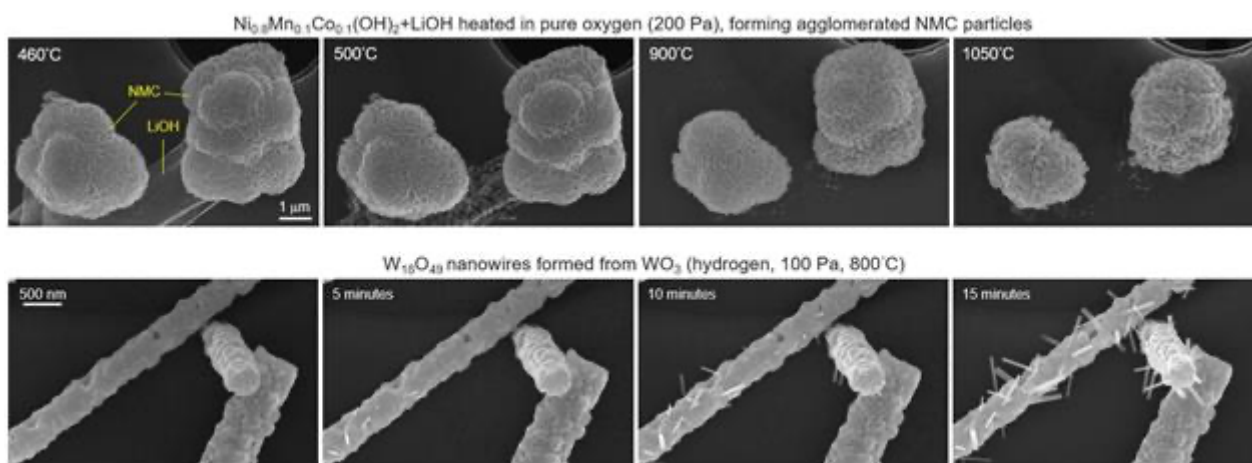
- 1) The capacity and lifetime of NMC cathode in Li-ion battery depend on the parameters of the high-temperature lithiation process. The MicroReactor can be used to follow morphological changes of the NMC particles which indicate the state of lithiation. An example of a possible way of lithiation process, that uses LiOH as the source material, is shown in the graphics. A pure oxygen environment was selected in the MicroReactor to remove the hydrogen from the final cathode material.
- 2) The growth of tungsten suboxide W18O49 nanowhiskers from WO₃-SiO₂ nanofibers was studied in the MicroReactor [1]. Reduction of the WO₃ in nanofibers was possible at 800°C in a hydrogen environment (100 Pa). The tunability of redox properties, thermal stability, and large surface area make tungsten suboxides promising materials for applications in energy storage systems.
- 3) Tungsten disulfide is a 2D material with unique properties applicable in many fields including electronics, catalysis, and energy storage. A modified pumping system of the Scios DualBeam equipped with MicroReactor enabled the injection of hydrogen sulfide & hydrogen mixture which was essential for the successful sulfidation of a sample containing W18O49 nanowires. Using a combined in-situ SEM and ex-situ TEM analysis, it was possible to explain the mechanism of WS₂ synthesis from tungsten suboxides for the very first time [3].

Conclusion

The three presented examples demonstrate novel applications of the MicroReactor in SEM. The second example proved process cleanliness sufficient for sample reduction at high temperatures. The creation of this abstract proves the possibility of safe work with dangerous gases in the third

example, which at the same time demonstrates the possibility of exploring the fundamental behavior of chemical processes.

In addition to the conclusions summarized in [1] and [3], it can be stated that in situ SEM equipped with the MicroReactor is a useful complement to the more widespread TEM in-situ techniques, which can bring new insight with several benefits. SEM excels in capturing reaction kinetics at a larger scale and provides topographical information in the surface-sensitive signal of secondary electrons. The presented technique can further be combined with ex-situ TEM analysis or with ETEM, both on the same MEMS chip that is used in SEM.



Keywords:

In-situ SEM, MicroReactor, batteries, WS2

Reference:

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235

Continuous EELS spectrum imaging of nano-droplet crystallization heterogeneity

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Poster Group 1

Background incl. aims

Electron energy loss spectroscopy (EELS) is a powerful technique for characterizing nanomaterials; a number of materials properties can be extracted from the information-rich spectra. One application is nano-thermometry, where the local temperature of individual metal nanoparticles can be measured by a precise determination of the plasmon peak position [1]. As thermal expansion increases a particle's volume, the density of electrons decreases, and the energy loss of the plasmon peak shifts to lower energies. This same approach can be used to detect melting and crystallization, which result in even larger changes in the electron density. Continuous acquisition of EELS data enables precise determination of the melting and crystallization temperatures of individual particles. Using the new in-situ EELS spectrum imaging features of the Continuum GIF, a continuous series of drift-corrected spectrum images can be acquired over an ensemble of particles, and the melting and crystallization behavior of each one independently monitored. This would be more difficult or impossible with other techniques such as TEM imaging, diffraction, or 4DSTEM.

Methods

In this work, we show how a series of EELS spectrum images can be acquired and processed along with the temperature data from a MEMS-based heating holder from DENSolutions. With modern fast detectors and spectrometers, spectrum images with thousands of spectra can be acquired in less than a second, making continuous in-situ spectrum imaging feasible. The holder temperature data is automatically synchronized and correlated with EELS spectrum image data. We also show how the entire series of in-situ EELS spectrum images can be rapidly fit using the built-in NLLS tools in DigitalMicrograph, yielding series of synchronized fit maps, as seen in Figure 1. After summing the EELS spectra over a single nanoparticle, plots of the peak position over time can be generated, and even plotted against the nominal temperature from the holder in scatterplots in DigitalMicrograph. The plasmon peak position within each particle indicates whether the Sn is melted or crystallized at that time.

Results

This new in-situ EELS spectrum imaging capability has been applied to a Sn nanoparticle sample which was oscillated above and below its melting temperature with varying ramp rates. Spectrum images were recorded at a rate of 1 frame every 1.54 s (2000 spectra/s). Watching the maps of plasmon position over time reveals that while all the Sn particles crystallized during most cycles, and most particles crystallized during every observed cycle, some particles occasionally did not crystallize even though surrounding particles did. Images and 4D STEM maps of the particles after the in-situ recording do not indicate a clear difference between a particle that always crystallized and the particles that sometimes did not. Some variation could be the result of random chance, as the nucleation and growth of a crystalline nanoparticle from a nano-droplet is governed by both thermodynamics, which would indicate that the particles should all crystallize at the melting temperature, and kinetics, which stipulates that nucleation times for an ensemble will have some distribution. However, there are only 3 particles (of 11 in the field of view) which don't always re-crystallize, and one of them remains melted during 4 cycles, which seems unlikely to be due only to random statistical fluctuations in nucleation time.

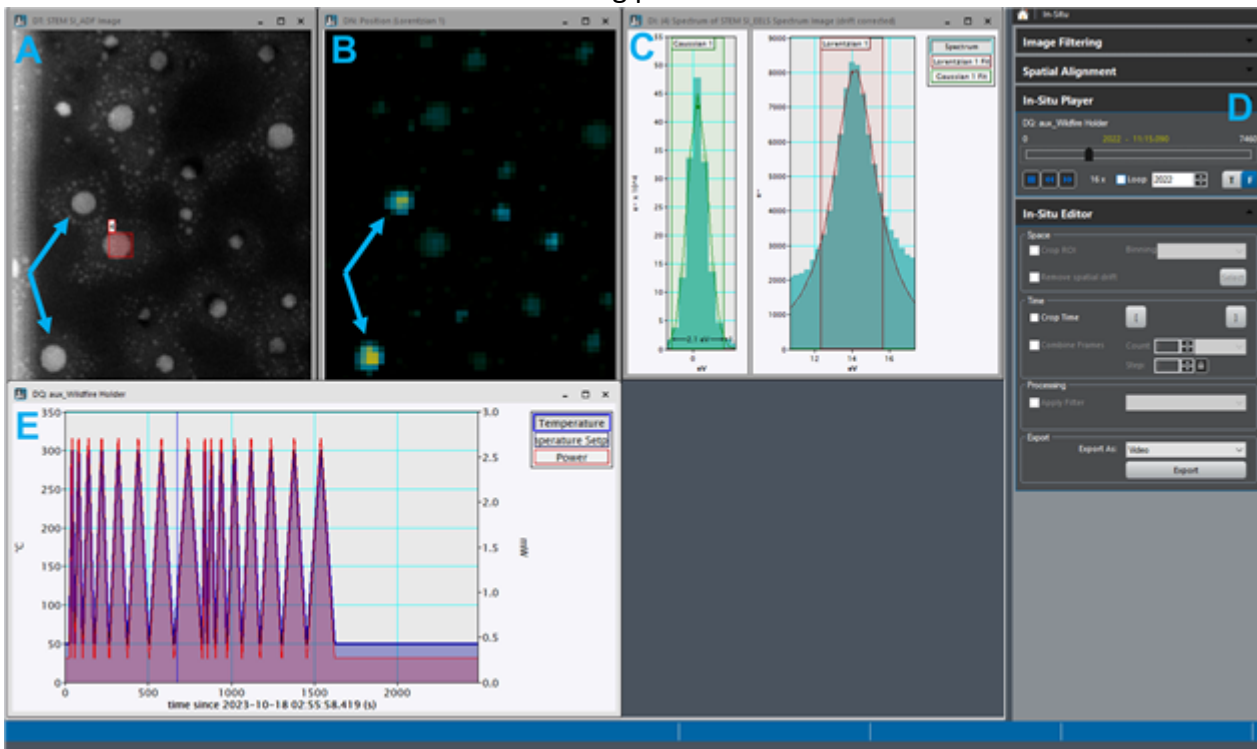
This behavior would be significantly more difficult to observe with TEM or STEM imaging, where the visibility of lattice fringes is dependent on the orientation of the nanoparticles. It would also be

challenging with standard diffraction techniques, where the crystallinity of multiple particles could not be independently and simultaneously observed. Continuously acquired 4DSTEM could be used, but this requires more data to be stored, and the analysis is more complex, especially if there are other small crystallites (oxides, etc.) which overlap the droplets, as there are here.

Conclusions

This heterogeneous and stochastic behavior at the nanoscale can only be observed with high spatial and temporal resolution. In-situ electron microscopy, and specifically in-situ EELS spectrum imaging is an excellent technique for exploring these dynamics.

Figure 1: One frame from a screen-capture video showing playback of the in-situ EELS spectrum image dataset. A) Simultaneously acquired dark field STEM images. B) Maps of the plasmon peak position. Arrows indicate 2 particles which have failed to re-crystallize despite super-cooling them to 50 °C. C) Live fit of the zero loss peak and plasmon peaks from the red “picker tool” region indicated in A. D) In-Situ Player which plays back and synchronizes all displayed in-situ dataset components. E) Automatically acquired and synchronized temperature data from the DENSSolutions heating holder used to heat the Sn above and below its melting point of 232 °C.



Keywords:

EELS
 In-Situ
 nanoparticle
 crystallization
 melting

Reference:

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376

Electrochemistry in LP-EM & Effects Induced by Irradiation of Metal Electrodes

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Poster Group 1

Background incl. aims

Electrocatalytic processes are a prerequisite for efficient decarbonization, i.e. by providing green energy via green H₂ synthesis or chemical precursors via CO₂ upconversion. However, this requires a profound understanding of these processes and a complete characterization of the materials employed in these technologies to reveal and prevent potential degradation mechanisms. Nowadays, in situ characterization techniques that use irradiation sources such as electrons or X-rays gained interest since mechanisms can be temporally and spatially resolved giving insights into the atomic scale of such complicated electrochemical reactions. [1]

The challenge that remains when using these techniques is the inevitable interaction of the irradiation source with the specimens in study. An effect widely studied is the generation of radiolytic species that alter the chemical environment, whether evolving beam-induced redox chemistry, or altering the solution/electrolyte acidity. [2] However, a so far overseen aspect when performing liquid-phase electron microscopy (LP-EM) experiments is the design of the three-electrode setup used for these experiments.

A common setup consists of utilizing noble metals like platinum (Pt) as working, counter, and reference electrodes. By having this configuration, effects like increased inelastic scattering, galvanic corrosion effects [3,4], changes in electrochemical response by variation of electrolyte flowrate, or interferences on the reference electrode signal [4] have been suggested. These effects need to be understood and considered as unrelated to the electrochemical reactions to avoid misinterpretations as degradation mechanisms.

Methods

To investigate into these proximity effects, 10 mM silver nitrate (AgNO₃) solution flowed (0.8 μL/min) through a patterned Pt three-electrode microchip in a DENSsolution Stream system. The specimen was constantly irradiated with a Thermo Fisher Scientific Talos F200i at 200 kV acceleration voltage in STEM mode (dwell time of 2 μs, and beam current of 533 pA). The Pt working electrode was biased until electrochemically Ag dendrite growth was observed and then stopped to observe the evolution of the process.

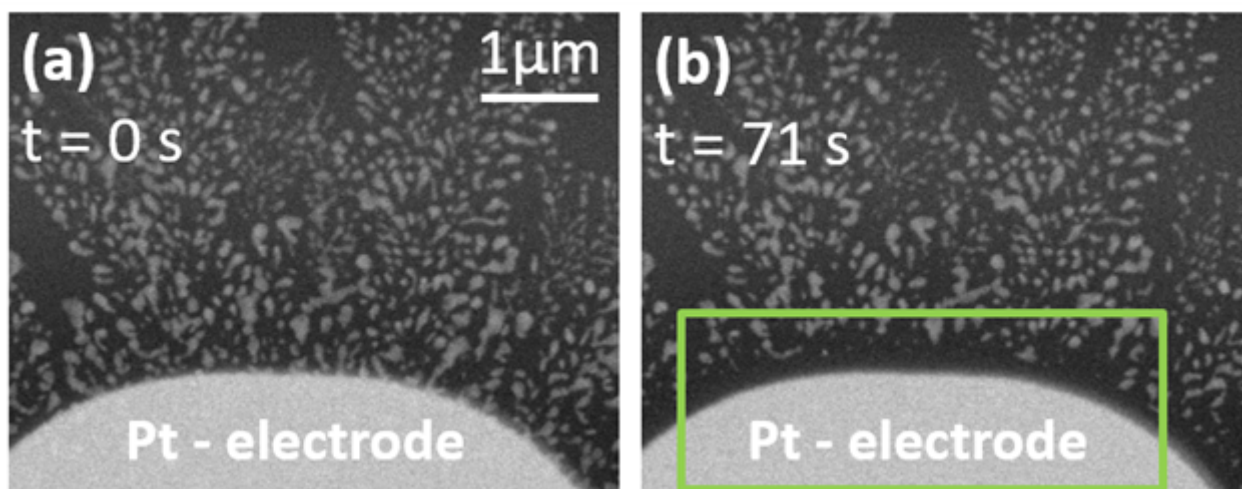
Results

Our work reveals that electrochemically grown Ag dendrites etch radiolytically as function of electrode distance. Particularly, the structures closest to the working electrode showed an accelerated dissolution (Figure 1: (a) Electrochemically grown Ag dendrites at time = 0 s, (b) Radiolytically etched Ag particles at time = 71 s, green area marked showing accelerated Ag dissolution when closer to the Pt working electrode.). This is supported by DSSIM analysis [5].

We discuss several possible mechanisms, including secondary electron-based local dose rate increases, Pt-catalyzed generation of oxidative species, as well as galvanic corrosion. Additionally, we report irradiation-driven potential overshoots when irradiating in the proximity of the reference electrode during electrochemical experiments.

Conclusion

In summary, we explore effects associated with the proximity and irradiation of the electrodes to further increase the control over and understanding of in situ analysis of electrochemical processes.



Keywords:

LP-EM, electrode-irradiation effects, galvanic corrosion

Reference:

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433

In situ size dynamics and manipulation of nanoparticle interaction under electron beam irradiation

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Poster Group 1

Background

The size-dependent properties of gold (Au) nanoparticles (NPs) have unique applications in various fields including science and technology ranging from environmental sensing and catalysis to drug delivery and biomedical imaging due to their excellent catalytic, electronic and optical properties. The practical applications of AuNPs in all fields usually require external stimuli, such as electron beam irradiation, temperature variations and mechanical compressions, which provide a further understanding of dynamics including the influence of kinetics of nanoparticle transformations and thermodynamic stability. However, such external stimuli induce structural transformations in AuNPs depending upon their intensity. In recent years, several studies have been conducted to understand the dynamic behavior of AuNPs under the control conditions to exploit their full potential and broaden their applicability in diverse fields. For this purpose, the comprehensive use of transmission electron microscopy (TEM) has already been implemented to study real-time in situ dynamic changes in NPs. The most common coalescence phenomenon is well documented in the literature, nonetheless, the nanoparticle size dynamic and repulsion phenomenon are considered here as a background for the knowledge gap.

The use of high-intensity electron beam irradiation in TEM outcomes in a beam-induced phase transition, surface charging, ionization and defects, providing insights to observe structural changes in individual metal NPs and interactions between a pair of coupled metal NPs at the nanoscale [1,2]. This study aims to investigate the dynamic behavior of AuNPs under the influence of electron beam irradiation including the interaction between closely placed a pair of AuNPs resulting in coalescence or repulsive behavior between them. The study made use of different surface substrates, such as carbon and silicon nitride (SiN) to additionally explore the effect of substrate-nanoparticle interactions. Furthermore, we target our focus on the interaction between different coupled NPs induced by surface charges, electrostatic forces, interparticle distance and size dynamics. By accomplishing these objectives, we aim to contribute to a deeper understanding of NPs manipulation for their applications in advanced photonic and plasmonic nanodevices.

Methods

Different-sized AuNPs on carbon and SiN substrates were irradiated under a controlled dose of an electron beam using TEM. In situ imaging was acquired using the OneView Gatan camera system to monitor dynamic changes in AuNPs.

Results

Several intriguing phenomena were observed upon the irradiation of the electron beam. Firstly, the individual spherical NPs showed remarkable structural transition, involving the structure transformation, for example, from face-centered cube (fcc) to a decahedral facet structure. The structural changes observed with atomic diffusion and structure reconstruction across the substrate are due to the transferred energy from the electron beam, during the electron-matter interactions. Furthermore, two more phenomena were observed in the case of coupled AuNPs, such as coalescence and repulsion between a pair of coupled AuNPs under an electron beam depending on the electron dose, interparticle distance and size dynamics. Coalescence is a favorable phenomenon

which is initiated with the formation of a neck-like structure with the lattice reorientation between two NPs in order to transform to a more stable structure by minimizing the overall surface energy and generating more localized plasmon at the particle-particle interface [3,4]. On the other hand, the repulsion phenomenon is also affirmative under the electron beam interactions governed by surface charge dynamics and electrostatic forces on a carbon substrate, which play a pivotal role in stability and dispersion under electron beam irradiation.

Conclusions

This study provides valuable insights into nanodynamic behavior of AuNPs under the influence of electron beam interaction to explore different nanoscale phenomena on carbon and SiN substrates. The dynamic behavior of AuNPs showed the structural transformation, coalescence and repulsion phenomena on carbon substrate under the electron beam irradiation. Contrarily, strong adhesive interaction between AuNPs and SiN substrate restricted the NPs diffusion across the surface leading to the melting of NPs under electron beam irradiation due to the transferred energy, consequently confining the coalescence and repulsion phenomena. Whereas heating treatment favored the coalescence phenomenon on SiN substrate. Furthermore, the dynamic behavior of AuNPs was recorded as perturbation and rotation of NPs on both substrates under electron beam effects. These outcomes contribute to a deeper understanding of AuNPs size and surface dynamics to manipulate for various applications, such as in material science including nanodevices, and nanotechnology. Future research directions may consider the substrate-nanoparticle interaction in depth using controlled experimental and computational methods.

Keywords:

Structure transformation, Coalescence, Repulsion, Size-dynamics

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443

Development of simple image processing for in-situ TEM toward live processing

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Poster Group 1

Background incl. aims

In-situ transmission electron microscopy (in-situ TEM) has become an essential tool for studying dynamic phenomena at the nanoscale [1]. Observing nanoscale phenomena with in-situ TEM allows us to understand the mechanism in more detail, which leads to improving material properties or increasing the process efficiency. However, most of the information is available only after a long time of analysis, which ends up as a passive approach. To actively investigate the phenomena, more information should be extracted during the in-situ experiment to manage the stimuli in real time. Live processing during the in-situ TEM experiment can allow to overcome this limitation by actively controlling the stimulus conditions according to the observed features, thus allowing dynamic adjustments during the experiments. Achieving live processing requires two critical components: 1) establishing real-time communication channels between the TEM, the in-situ stimuli, and the processing server, and 2) developing fast and efficient image processing algorithms capable of handling the high throughput of data generated during in-situ TEM experiments. Until now, artificial intelligence (AI) has not been able to help with live processing due to the large amount of computing power and time required. While the establishment of real-time communication channels requires cooperation with TEM manufacturers, this paper focused on the development of image processing algorithms suitable for live processing.

In this work, we present the development of simple but effective image processing techniques suitable for live processing in in-situ TEM. Three cases of segmentation from electrochemical in-situ TEM experiments were shown as: (Case 1) plating and stripping of Zinc (Zn), (Case 2) dendritic growth of Zn, and (Case 3) particle-like plating and stripping of Copper (Cu) [2, 3]. Through these case studies, we demonstrate the ability of simple image processing to understand electrochemical phenomena and its potential for applications.

Methods

a) Performing in-situ electrochemical TEM experiments

In-situ Liquid TEM holder (Stream, DENSsolution) assembled with 3-electrode Micro-Electro-Mechanical System (MEMS) chips was used for experiments. In case 1, Pt electrode MEMS chip and 0.1 M ZnSO₄ solution (flowing) were used and cyclic voltammetry (CV, -1.5 V ~ +0.8 V for 0.01 V/s scan rate) was applied. In case 2, Pt electrode MEMS chip and 0.1 M ZnSO₄ solution (non-flowing) were used and chronopotentiometry (CP, 5 μ A for 10 seconds) was applied. In case 3, TiN_x electrode MEMS chip and 0.02M CuSO₄/0.01M KH₂PO₄ solution (flowing) were used and chronoamperometry (CA) with 4 cycles (one cycle: +1.5 V for 15 seconds and -1.5 V for 15 seconds) was applied. Case 1 and 2 were monitored at STEM mode and case 3 was monitored at TEM mode.

b) Developing simple image processing methods dedicated to in-situ TEM

All the image processing methods are developed as python codes. To reduce the noise level, a gaussian filter was applied as pre-processing. Key strategies are 1) subtraction of the reference image

(pure electrode) from target image (during experiment) to extract the information changes and 2) thresholding the subtracted image to binary-segmenting as feature and background. Especially case 2, the subtraction was performed between images with 1 second difference, in order to emphasize the fast growth of dendrite within 1 second. After the segmentations, the deposition information such as deposited area was numerically extracted and plotted.

Results

In case 1 (Figure 1a), Zn plating and stripping phenomena were recorded with CV stimuli. On the recorded STEM images, the plated Zn is well visible, but the brightness of the plated Zn looks similar to the rectangular Pt electrode on the right side. After the simple image processing as described in methods, the plated Zn is clearly visible without Pt electrode and the area of plated Zn can be measured easily. After measuring the area throughout the whole CV process, the plated Zn area can be synchronized with the CV stimulus data, which leads to a quantitative understanding of the phenomena.

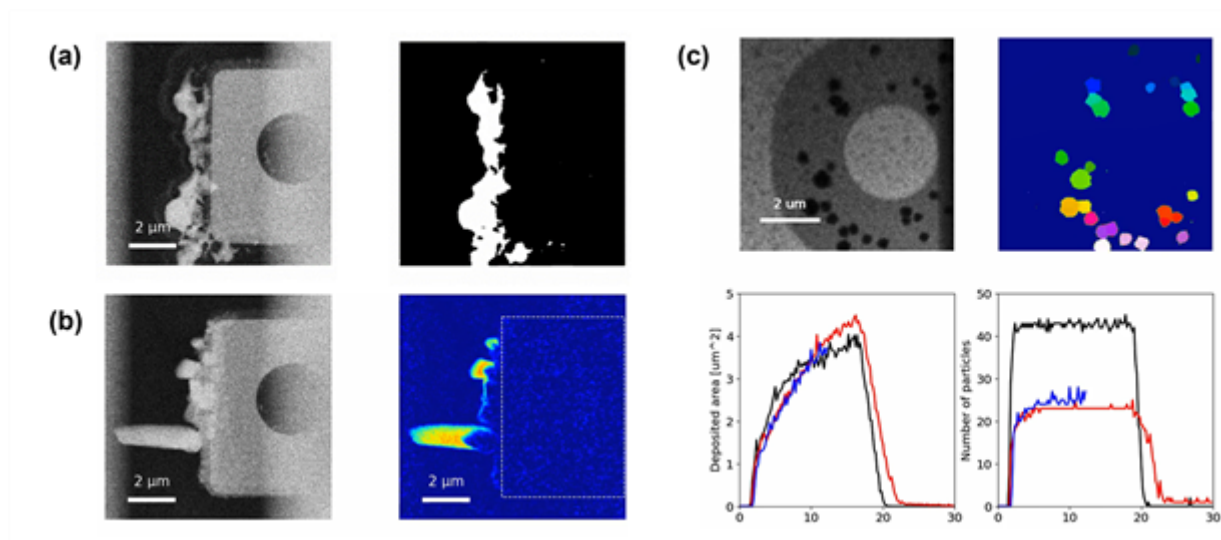
In case 2 (Figure 1b), Zn dendritic growth was recorded with CP stimuli. From the video, a dendritic growth took only a few seconds, so the information related to the growth rate is more important than the amount of growth. By subtracting the 1-second difference between frames, the grown dendrite is visualized in 1 second, which can directly show not only how fast the dendritic growth is, but also which direction is preferred. In this case, Zn dendrite growth occurred to the left where the counter electrode is located.

In case 3 (Figure 1c), Cu particle-like plating and stripping was recorded with cyclic CA stimuli. On the recorded TEM images, plated Cu particles are well visible on the top of the electrode (round shape with hole), but small dots are also visible at the outside of electrode. Large Cu particles on the top of the electrode are formed based on electrochemical deposition and small Cu particles outside of electrode are electron beam induced deposition. To focus on electrochemical deposition, the only electrode area was selected to further particle segmentation. After the image processing, each individual Cu particle was segmented and could be tracked during the plating and stripping process. The area and number of particles were plotted with a time scale to study the plating and stripping phenomena.

Conclusions

In-situ TEM has been enabled to observe countless phenomena in nanoscale, but quantitative information was very limited due to huge amount of dataset which cannot be handled by human. This paper showed that the bunch of quantitative information can be extracted from recorded in-situ TEM video by simple image processing. We believe that simple image processing will allow to actively investigate the phenomena at nanoscale by correlating the observed feature and applied stimuli in real time.

Figure 1. Examples of image processing from in-situ TEM dataset. (a) STEM image and segmented image of metal deposit. (b) STEM image and reconstructed image of metal dendrite growth within 1 second. (c) STEM image, segmented image of particle shape deposits and graphs about deposit area and number of particles vs. time. [2, 3]



Keywords:

in-situ TEM, Live, Image processing

Reference:

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475

Electron microscopy and X-ray techniques correlative in situ studies in microfluidic conditions on hybrid perovskites

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Poster Group 1

Hybrid organic-inorganic perovskites (HOIP), a class of materials with a cubic unit cell (ABX₃) possess remarkable physical and chemical properties and have aroused growing interest in the scientific community in the last decade. The A-cation, at eight corners of the cube, is surrounded by twelve X-anions (mainly halides, Cl⁻, Br⁻, I⁻), while the B-cation (typically divalent metal ions such as Pb²⁺, Sn²⁺ or Cu²⁺) is located at the body center surrounded by six X-anions in an octahedral [BX₆]₄-cluster. When the A cation is replaced by methylammonium cations (MA=CH₃NH₃⁺), three-dimensional hybrid organic-inorganic structures are obtained, known as 3D hybrid perovskites, with potential applications in solar cell technologies. Their high power conversion efficiency (PCE), together with their low-cost and scalable, solution-based fabrication processes lead to intense research efforts towards their industrialization. Despite these advantages, 3D perovskite solar cells also face significant challenges. The long-term stability of these materials remains a major concern, as they can be sensitive to moisture and other environmental factors, leading to a premature degradation. In this context, there has been growing interest in 2D HOIPs. These materials include larger organic cations as hydrophobic spacers, isolating the inorganic metal halide octahedra and leading to improved stability compared to their 3D counterparts. A wide variety of structures can be obtained for these materials, depending on the organic or inorganic cations and the synthesis conditions. Indeed, their synthesis in solution implies complex chemistry, with pre-organization, nucleation, reorganization and precipitation. Controlling the properties of these materials need a precise control over their structure, hence over their synthesis pathways.

For a better understanding of the synthesis of HOIPs by ligand assisted re precipitation (LARP) and to control their structures and properties, we developed a new approach for observing the structural evolution of 3D/2D lead halide hybrid perovskites based on a time-resolved acquisition protocol of the structural data. By combining in situ liquid transmission electron microscopy (TEM) and X-ray absorption techniques, we can monitor in real time the birth and the structural and chemical evolution of the different phases in well-controlled and realistic conditions and have a better understanding of the associated mechanisms. Specific microfluidic devices were developed for this work, which were used to perform in situ X-ray absorption studies and can be applied to other X-ray techniques as well. This new device reproduces the precipitation of 3D/2D lead halide hybrid perovskites under X-ray in particular for X-ray absorption near edge structure (XANES), for Extended X-ray Absorption Fine Structure (EXAFS) and for Small-angle X-ray scattering (SAXS) analyses. This micro fluidic chip has been designed to be versatile and adaptable to the specific needs of synthesis. The internal microfluidic pathway can be easily changed in design, from a T to observe the interface between two fluids, or a mixer to reproduce the conditions required for precipitation. By combining this information with those obtained from in situ liquid TEM with the Protochips technologies Poseidon AX and X-ray diffraction, we propose mechanisms for the formation and structural transition of different phases of this family of perovskites. This method highlighted the importance of studying the precursor solution to the LARP method, at which stage an atomic arrangement was found. This indicates that the synthesis of HOIPs begins before precipitation with the formation of a forerunner atomic structure of the intermediate phase. We will also show how the method presented could be applied to the study of a variety of nanomaterials under in situ liquid conditions.

Keywords:

perovskite, insitu TEM, microfluidic device

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Transfer of Nanomaterials for in-situ TEM with electrical Currents

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Poster Group 1

Background incl. aims

In-situ transmission electron microscopy (TEM) has evolved to be a crucial tool for studies of dynamic processes in a large variety of specimens. While numerous examples exist that use gaseous/liquid environments, heating, biasing or the application of a mechanical force, studies in which the electrical current (and not bias) has been used as external stimulus are scarce. [1,2] A possible reason is the necessary controlled contacting of the specimen, which is challenging, especially for nanomaterials that need to be kept free from any source of damage and contamination. Here we present a preparation technique that allows a clean and almost damage-free preparation to focus on the materials during the application of electrical currents inside the electron microscope. [3]

Methods

The key element of the process is a holey silicon nitride membrane, which supports the nanomaterial during the transfer with the focused ion beam (FIB) technique using Ga⁺ ions. In brief, the specimen is first prepared conventionally on a TEM grid made of such a holey silicon nitride membrane (PELCO). In a TEM analysis, a suitable individual nanomaterial can be selected, as exemplarily shown in Figure A for a nanotube (NT) and a flake made of the misfit-layered compound LaS-TaS₂. [4] The grid is then loaded into a dual-beam (SEM-FIB) instrument and the nanomaterial with the supporting membrane is transferred to a microchip using a microneedle and FIB induced deposition (FIBID) of Pt/C (Figures B and C). The properties of the silicon nitride facilitate easy contacting of the membrane to the contact pads of the chip by FIBID. Finally, the membrane is removed in the central part to leave the nanomaterial as only conductive bridge.

Results

Using the above-described transfer technique, we have prepared a range of different devices based on nanomaterials and evaluated in detail the transfer quality. Figure D shows a HRTEM image of the transferred LaS-TaS₂ (NT and flake) sample revealing no contamination or charging. The limits of the methods were tested with a monolayer of WS₂, which was successfully transferred and revealed that Pt/C contamination during FIBID is kept well below a monolayer. For 1D nanomaterials, Ga implantation can be kept to zero, while for 2D materials or thin films, a small amount of Ga is implanted at the edge of the specimen in the final step of removing the membrane in the central part. We will present exemplary experiments conducted on different prepared devices.

Conclusion

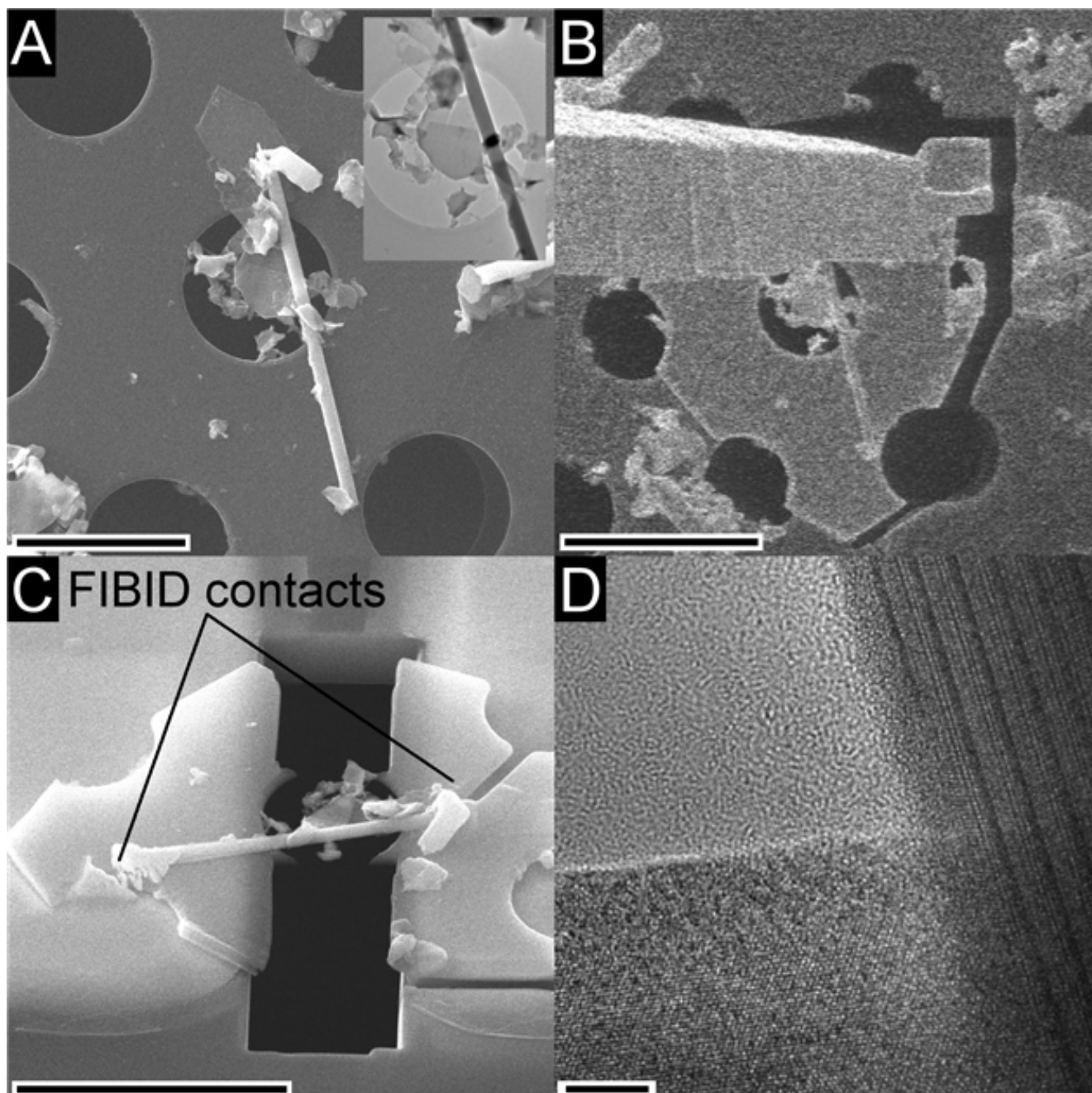
The development of a support-based transfer and contacting procedure of individual nanomaterials to microchips, e.g. used for in-situ TEM investigations, allows an almost artifact-free preparation of nanomaterial specimens for electrical in-situ TEM. Suitable nanomaterials can be selected by previous TEM analysis and correlative microscopy techniques. The resulting devices can be used to electrically characterize the nanomaterials and to dynamically study the effect of an electrical current on the sample. This includes Joule heating, which can be used to heat samples to extremely high temperatures, not reachable by standard heating in-situ TEM studies. Further possible investigations concern electromigration, electrical failure analysis or EBIC. In addition to in-situ TEM, the preparation method can equally be used to prepare devices on related microchips.

Acknowledgments

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Figure caption:

(A) SEM image of LaS-TaS₂ nanotube and flake. Inset shows a low-magnification TEM image of identical sample position. (B) SEM image of micro-needle holding membrane and nanomaterials after contacting and cutting free. (C) SEM image after milling of membrane in hole area of the chip with nanomaterials forming the only bridge between contacts. (D) HRTEM image of a flake and a nanotube (shown in (C)) after transfer. Scale bars are (A) 2 μm , (B,C) 5 μm , and (D) 5 nm.



Keywords:

in-situ-TEM, nanomaterials, sample preparation, focused-ion-beam

Reference:

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535

Novel polymer thin film fabrication for graphitization studied by in situ transmission electron microscopy

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Poster Group 1

Due to its excellent physical, chemical and electrochemical characteristics, pyrolytic carbon has emerged as a promising material for various technological applications [1]. Pyrolytic carbon can be obtained through the pyrolysis of a polymeric carbon precursor under controlled conditions at high temperatures and in inert atmosphere. By tuning the pyrolysis conditions, the hybridization of carbon atoms and thus the physicochemical properties of the derived carbon can be tailored. Although some researchers have attempted to investigate the graphitization process in atomic scale, a comprehensive understanding remains elusive. Transmission electron microscopy (TEM) is well-suited for investigating the graphitization of polymer thin films during the thermal treatment process at the nanoscale [2]. Indeed, TEM offers the advantages of in situ analysis capabilities which can reveal the nanostructure of pyrolytic carbon during the pyrolysis process. However, the preparation of polymer thin film samples for TEM remains a challenge. This work presents the microfabrication of suspended polymer thin film structures on MEMS-based TEM heating chips (DENSolutions Wildfire), by two-photon polymerization (2PP) 3D printing technology [3]. We also report the results of the in situ TEM studies for tracing the graphitization of pyrolytic carbon.

A Nanoscribe Photonic Professional GT+ system from Nanoscribe was used to fabricate suspended polymer thin films using DENSolutions chips as substrate. The microfabrication of thin films was done by direct laser writing of IP-Dip photoresist using 2PP with a Plan-APOCHROMAT 63×/1.40 Oil DIC objective. The optimized printing parameters were a laser power of 50%, a scan speed of 12000 $\mu\text{m/s}$, a hatching distance of 0.4 μm and a slicing distance of 0.1 μm . After printing, the samples were developed by a 20 min immersion in propylene glycol monomethyl ether acetate (PGMEA), followed by 20 min immersion in isopropanol. Finally, the structures were left to dry horizontally at room temperature.

TEM was performed with an FEI Titan 80–300 environmental transmission electron microscope. The microscope was operated at 300 kV at 10⁻⁸ Pa. In situ TEM was carried out with a TEM heating sample holder (Wildfire, DENSolutions). Images were recorded on a Gatan OneView camera at an exposure time of 0.2 s. Images were post-processed using DigitalMicrograph (Gatan, Inc.).

To fabricate a thin film for visualizing the graphitization of carbon in the TEM, several designs and pyrolysis conditions were studied and optimized before selecting the optimal ones. The dimensions and integrity of the structure post-pyrolysis were assessed using SEM and the nanostructure of the resulting carbon was investigated by TEM. Based on these preliminary tests, we identified favorable parameters to resolve graphitic domain formation in the TEM. The identified conditions are a thin film with a thickness of around 700 nm pre-pyrolysis, a pyrolysis sequence reaching a maximum temperature of 1300°C and a minimum of 2 hours of dwell at this temperature. The final thin film design is presented in Figure 1a. The sample consists of a suspended ribbon with a center through-hole to facilitate imaging of the suspended thin film all around the edge of the ring. The central ring is 700 nm thick for TEM imaging (in dark grey in Figure 1a) while the surrounding ribbon is thicker (900 nm) to provide support and strengthen the overall structure (in light grey in Figure 1a).

Figure 1b & c show the structure after printing and after pyrolysis, respectively. From these images we see that the ribbon, the window, and the hole are well-defined both before and after pyrolysis.

Three of the in situ TEM micrographs acquired during the dwell at 1300°C, are presented in Figure 1d to 1f. The images are acquired every 30 minutes, with the beam blanked between acquisitions. The formation of oriented carbon microdomains is visible, and their nature as graphitic carbon is affirmed by the measured inter-layer distance of 3.3 Å, a characteristic feature of graphitic materials. An increase in the number of graphene stacking layers was observed over dwell time. It is worth noting that since the beam is blanked in between acquisitions, these observations are valid independently of the beam influence.

To conclude, we demonstrated the successful 2PP fabrication of suspended polymer thin films for in situ TEM studies, as well as the visualization of graphitization on these films during in situ TEM heating studies.

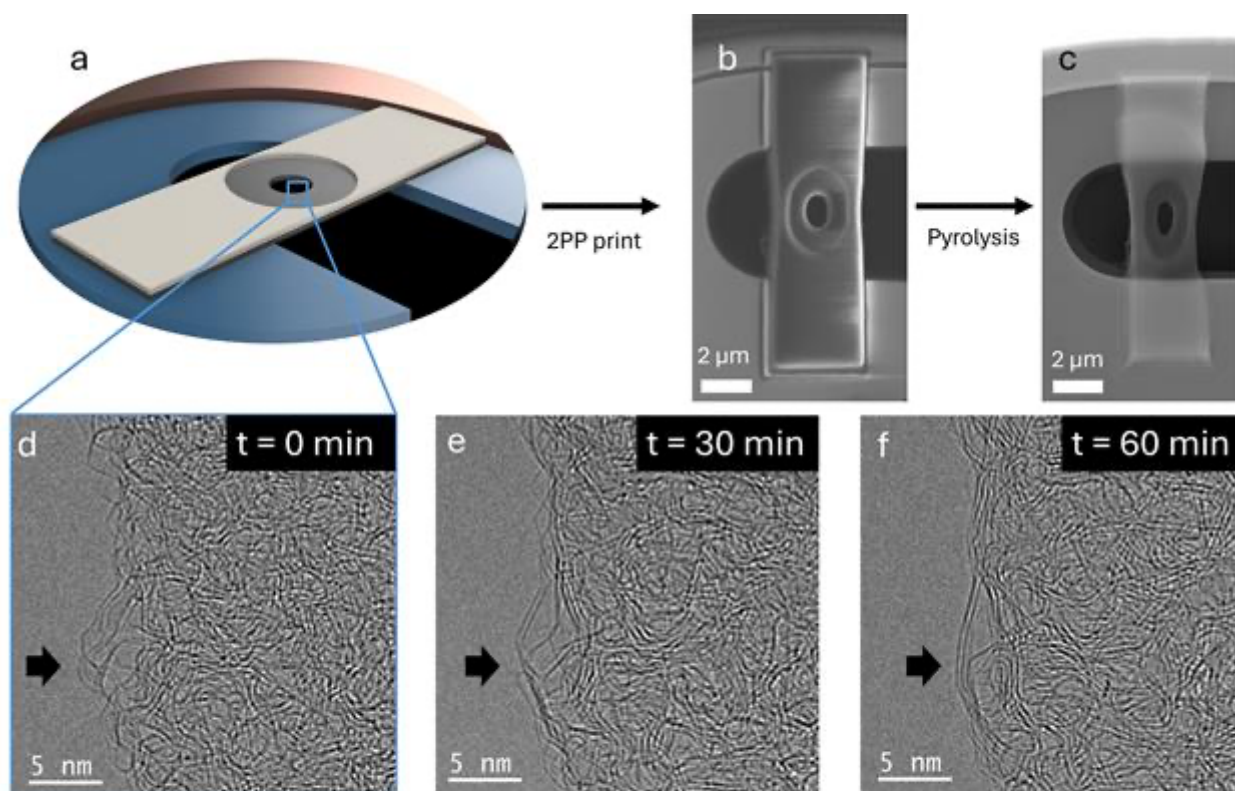


Figure 1: a) 3D design of the ribbon with the thin 700 nm window, in dark grey, for TEM imaging, b) SEM micrograph of the ribbon 3D printed with 2PP, c) SEM micrograph of the ribbon after pyrolysis, d) to f) Collection of TEM micrographs acquired every 30 minutes during the dwell at 1300°C, from the thin window on the ribbon, showing the evolution of the graphitization

Keywords:

in-situ TEM, pyrolysis, graphitization, two-photon-polymerization

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574

Multiscale characterization of plaster setting using operando multiscale liquid-phase Electron Microscopies

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Poster Group 1

Background incl. aims

Gypsum has been traditionally used as a building material, but can also be a model for the development of injectable biomaterials for bone substitution. Set plaster, or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is prepared by mixing dry hemihydrate powder ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) with water. Its properties as a solid binder are largely influenced by the setting reaction occurring when $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ dissolve and crystals of gypsum precipitate. It is well known that the resulting solid is formed by an interlocked network of gypsum needles and platelets, but the exact setting process is not well understood yet. The objective of our study is therefore to monitor the evolution of crystals and understand the entire setting process, using operando observations [1], using Liquid-phase scanning electron microscopy.

Methods

For Scanning Electron Microscopy (SEM) experiments, the hemihydrate powder is manually mixed with an aqueous solution containing 5.2 mM citric acid. Plaster paste is then deposited onto the window of a Quantomix cell placed in a Zeiss Supra 55VP SEM microscope. Such cells are indeed water - and airtight, and therefore plaster evolves under the same conditions as in real use, especially in terms of water-to-plaster ratio. Gypsum crystallization is followed by taking SE and BSE images every 30 s.

In situ Environmental Transmission Electron Microscopy (ETEM) experiments are performed on a Titan ETEM from FEI/TFS. The hemihydrate powder is dry deposited onto a grid covered with a holey carbon membrane, then placed on a cryo-holder from Gatan/Ametek. The temperature is slowly decreased to 0°C and once stabilized, the partial pressure of H_2O is increased until liquid water covers the hemihydrate particles.

Results

The dissolution of hemihydrates and crystallization of gypsum is followed operando in SEM. Image processing and analysis procedures are developed to segment the gypsum crystals and follow their growth vs time. Based on geometric information and the knowledge of the equilibrium morphologies [2], we propose an indexation of the crystal facets (see example in Figure 1). The growth rates of the different planes, including unstable ones, is measured.

In situ experiments in ETEM give a more precise view of the onset of gypsum nucleation, with the formation and evolution of facets at the nanometer scale.

Conclusion

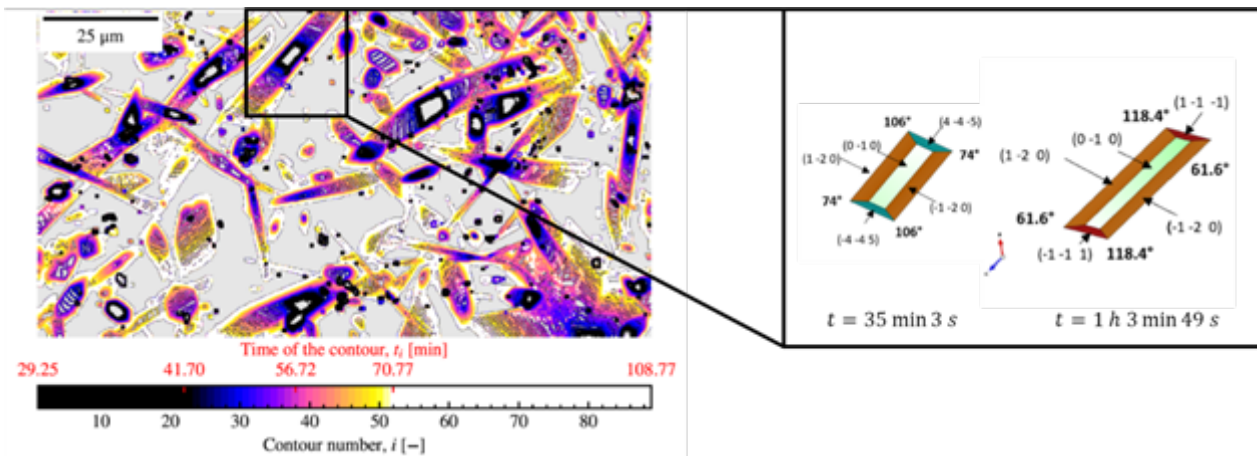
The use of liquid-phase electron microscopy at different scales allows the investigation of gypsum growth in a real plaster mixture. The formation of unstable facets and their transformation into stable ones are evidenced from the onset to full plaster setting. Moreover, the growth rates for all types of facets can be measured and compared with the few values found in the literature. The influence of several parameters is discussed (addition of a retardant, presence of a membrane, image acquisition conditions and irradiation damage) [3].

Acknowledgements

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Figure caption

Growth of the gypsum crystals during plaster setting and indexation of a crystal for two different times.



Keywords:

operando, liquid, crystal, growth

Reference:

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627

In situ TEM holder for liquid cell research with combined electrochemical and thermal stimuli control

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Poster Group 1

In situ (scanning) transmission electron microscopy ((S)TEM) experiments in liquid phase gain momentum due to the development of sandwiched MEMS-based samples carriers (e.g. Nano-Chips) – liquid Nano-Cells. Various stimuli like heating or biasing in liquid environments have been employed to study materials nucleation and growth [1], ion batteries [2], electrocatalysts [3] and more. The majority of the commercial in situ (S)TEM sample holders utilize only four electrical contacts that limit the combination of stimuli that the user can simultaneously apply. However, to mimic the real-world operation conditions in applications like proton exchange membranes, Zn-ion batteries, etc require combined application of thermal and electrical stimuli and thus, higher number of electrical signals.

In this work we present our new platform for in situ and operando environmental (S)TEM experiments. The heart of this platform is a newly designed holder with eight electrical contacts and multiple liquid inlets that allows the application of thermal and electrical stimuli next to liquid flow and mixing capability. The specially designed liquid Nano-Cells with eight electrical contacts contain a heater and four biasing (Working, Reference, Counter + 1) electrodes for combined electrochemical and thermal experiments. The holder has a removable tip that has a generic design and is compatible with different TEM vendors. Additionally, the design of the holder allows to rotate the tip making it suitable for both TEM and STEM operation.

We will demonstrate the capability of the holder in terms of TEM and STEM imaging, elemental analysis using EDS and 4DSTEM. We will show a few experimental examples of the new environmental operando system, including electroplating and stripping of metals as a function of temperature and the flow.

Keywords:

In situ TEM, liquid phase

Reference:

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811

Towards customized in situ TEM Chips for “device-like” geometries

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Poster Group 1

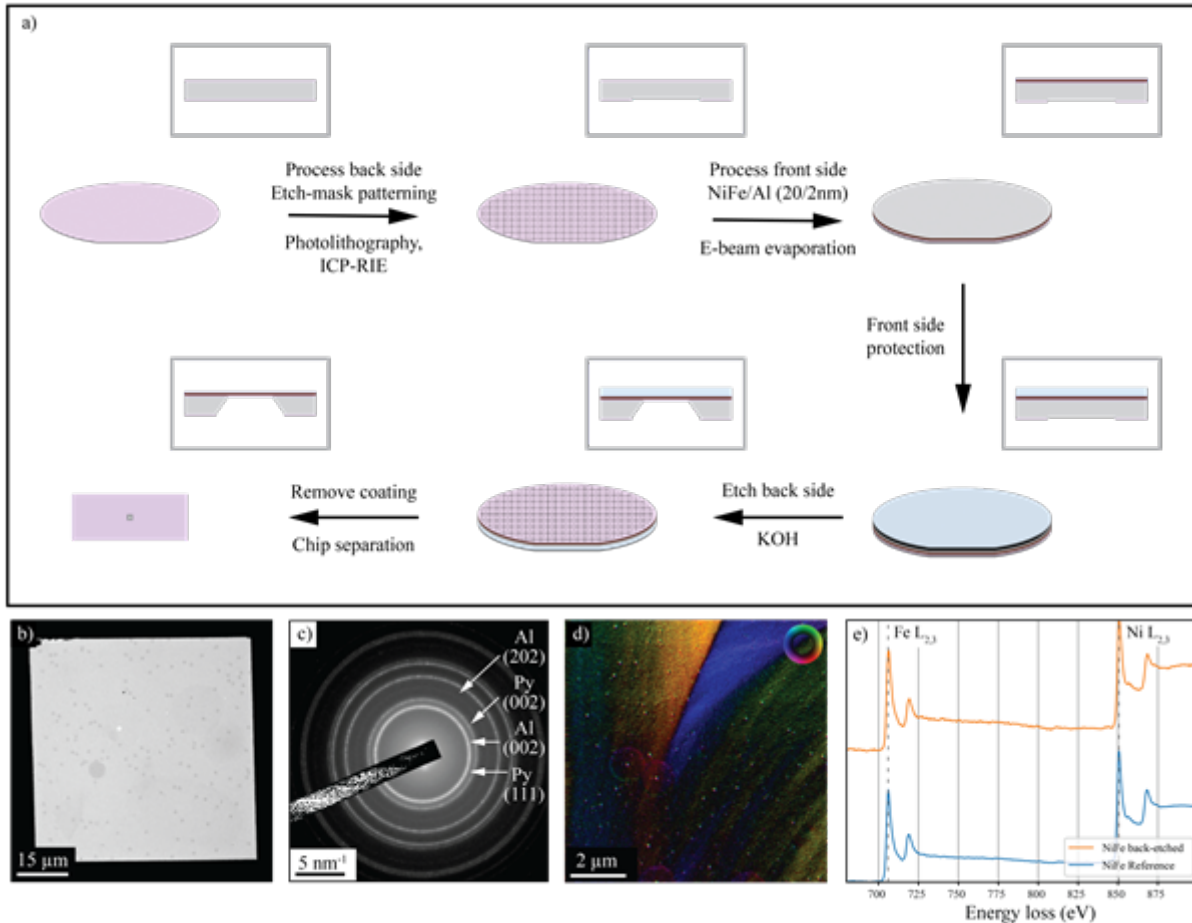
Functional nanostructures and thin films have applications within the next generation of memory storage, energy storage, quantum computers and sensor technology [1,2]. Their characteristic properties originate from the nano or even atomic scale, necessitating the combination of high-resolution techniques and imaging of functional properties to better understand their structure-property relationships. Scanning transmission electron microscopy (STEM) can be used to capture the structure, chemical composition, and functional properties of these materials.

For in situ STEM characterization, the material of interest must be transferred to an electron-transparent region of a TEM chip. For thin films, this means depositing it on the membrane of a commercial TEM chip, or alternatively, transferring it by FIB lift-out or similar techniques. However, for larger systems consisting of nano- or micro-sized structures relevant for prototyping of new device concepts, this quickly becomes challenging, as the field of view required for such geometries may be many times larger than what is feasibly prepared by plan-view FIB lift-out. An alternative approach would be to fabricate these “device-like” structures directly on the TEM membrane. However, performing advanced lithography steps on a fragile, pre-made, electron-transparent window involves a non-negligible probability of fracturing it. We aim to solve this by fabricating TEM membranes directly from the substrate, etching electron-transparent windows from its back side after processing the front side. Similar work has been performed on customizable TEM chips for nanowires [3], but here we aim to utilize this approach for specimens requiring a larger field of view. The outlook for a simple, reproducible, fabrication process is many, as the advantages stretch across customizable window sizes and tailored chip designs. Additionally, it may expand the type of material systems that can be studied in situ, as-grown and in-plane without the need FIB lift-out.

The first step in achieving a robust protocol for the fabrication of customizable TEM chips is to optimize the back-etch to release electron-transparent membranes. As proof of concept, back-etched TEM chips were fabricated for a simple ferromagnetic $\text{Ni}_{80}\text{Fe}_{20}$ thin film (Fig 1.). Starting with a double-side polished silicon wafer coated with 30 nm Si_3N_4 , the etch-mask was fabricated by patterning the Si_3N_4 on the back side of the wafer by photolithography and inductively coupled plasma reactive-ion etching (ICP-RIE). A 20 nm $\text{Ni}_{80}\text{Fe}_{20}$ thin film was deposited on the front side by electron beam evaporation, and thereafter protected by AR-PC 5040 protective coating. The electron-transparent windows were released by immersing the wafer in a KOH bath, and consecutive removal of the protective coating. TEM characterization of the windows shows successful fabrication, with the $\text{Ni}_{80}\text{Fe}_{20}$ retaining its ferromagnetic properties. This provides further evidence that the sample preparation was successful and that the front side was sufficiently protected from the KOH etch.

The next steps will focus on fabricating $\text{Ni}_{80}\text{Fe}_{20}$ nanomagnet arrays by electron beam lithography on a similar $\text{Si}/\text{Si}_3\text{N}_4$ substrate with wires for in situ biasing. As such, this presentation will also show the next steps towards doing in operando studies of magnetic device concepts. [4]

Figure 1: a) Schematic of the TEM membrane fabrication steps. The insets show the cross-section of the wafer. b-d) Low-magnification STEM image, SAED pattern, and STEM-differential phase contrast (DPC) image of the back-etched Ni₈₀Fe₂₀ TEM window. Some particle contamination can be observed on the back-etched samples. e) EELS spectrum of the back-etched Ni₈₀Fe₂₀ thin film against a reference Ni₈₀Fe₂₀ specimen.



Keywords:

STEM, in-situ TEM chip, nanofabrication

Reference:

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[4] The authors would like to acknowledge support from the Research Council of Norway through the Norwegian Micro- and Nano-Fabrication Facility, NorFab (295864), the Norwegian Center for Transmission Electron Microscopy, NORTEM (197405/F50) and In-situ Correlated Nanoscale Imaging of Magnetic Fields in Functional Materials, InCoMa (315475).

1018

Metal-Organic Chemical Vapor Deposition in a Transmission Electron Microscope

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Poster Group 1

Background incl. aims

Using environmental transmission electron microscopy, researchers can observe - with high resolution and in real time - transformations and reactions under realistic conditions. Such studies benefit from precise control, monitoring, and variability of ambient gas, potentially including multiple independently controlled species to which a sample is exposed at the same time. This represents a challenge for ETEM analysis and has required the design of systems that integrate the capabilities of advanced crystal growth instrumentation with the specific requirements of TEM to allow elevated sample pressure and temperature, as well as a better understanding how the environment influences the analysis and vice versa. To address these challenges, we developed an ETEM system based on a Hitachi HF3300S instrument, which is integrated with a metal-organic chemical vapor deposition (MOCVD) system designed for real-time investigation of crystal growth processes of semiconductor nanostructures[1].

Here, we demonstrate how the design of the ETEM-MOCVD instrumentation enables independent control of the gas composition and flow that reaches the heated sample region, as well as rapid adjustments of the gas supply. We focus on the implemented solutions used for controlling gas concentration and pressures in the system and at the sample region. Solutions for calibration and monitoring partial pressures as well as total pressure in the microscope and at the sample are presented and evaluated, together with pressure correction factors of the pressure gauges for nitrogen (N₂), arsine (AsH₃), and phosphine (PH₃). In addition, we explore the influence that the temperature and gas supply to the microscope itself have on imaging and analysis, and conversely, how the imaging via electron beam influences the experiment. Effects of temperature and gas environment on spatial resolution are quantified, and we also demonstrate and quantify how X-ray energy-dispersive spectroscopy (EDS) analysis is influenced by the local reactive sample environment.

Methods

The ETEM is based on an image corrected Hitachi HF-3300S 300 kV TEM, with additional ion pump and differential pressure aperture. The gas handling system is custom built but based on industrial standard mass flow controllers, pressure controllers and vapor concentration measurement units (HORIBA). Nine different gases are controlled via the gas handling system, primarily for III-V semiconductor growth: trimethylgallium (TMGa), trimethylindium (TMIn), trimethylaluminum (TMAI), trimethylantimony (TMSb), AsH₃, PH₃, nitrogen, hydrogen, and oxygen. Other gases are possible by either replacing any of the existing sources, or by using external gas delivery and leak valves. Heating is done using MEMS heating chips.

Results

The design of the gas handling system and particularly the ability to dilute the precursor species with additional high flow of H₂ allows for a very wide range of precursor flows and partial pressures to be achievable, spanning over four orders of magnitude (approximately 4×10^{-6} to 0.1 Pa of TMGa, or 7×10^{-5} to 2 Pa of AsH₃). These partial pressures are comparable to conventional MOCVD growth of binary semiconducting nanostructures.

Since the microscope is of an open design with local gas injection close to the heated area of the holder, a local higher pressure at the holder compared to the column pressure gauge location is expected. Using a MEMS heating chip as a pulsed Pirani gauge, we correlate pressure at the holder to the microscope column pressure. Depending on gas delivery method (via gas injection holder or side port injector) and holder tilt, pressure at the MEMS chip was found to be 1.6 to 2.8 times higher than column pressure gauge. If using additional lid on gas injection holder, pressure at the MEMS chip was found to be 200 times higher than the column pressure.

Achievable spatial resolution during gas exposure on a heated MEMS chip was estimated using Young's fringes. Measured resolution is slightly worse than the 0.86 Å achievable under optimized conditions[2], mainly due to stability of the holder and MEMS chip. Elevated temperature and gas exposure had a very minor effect on resolution.

Increasing temperature on the SiNx based MEMS chips, the thermal radiation of the chip increases. Such thermal radiation affects the EDS measurement mainly by increasing the strobe peak intensity, but at high enough chip temperature also energy shift of strobe peak and elemental peaks.

Conclusion

We present a system that merges an environmental TEM with an MOCVD setup for real-time study of crystal growth. The open holder design allows for a wide sample tilt range, quick gas switching, and various analysis techniques. The gas handling system replicates standard MOCVD conditions and is flexible for different gas pressures, flows, and precursor types. We found no significant effect of heating or gas pressure on spatial resolution, and minimal interaction of the electron beam with the gas.

Keywords:

ETEM, in-situ, MOCVD, semiconductor

Reference:

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1162

In-situ cryo-biasing heating TEM sample holder with full-range temperature control from -170°C up to $>1000^{\circ}\text{C}$

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Poster Group 1

Background

Traditionally in-situ TEM biasing, heating and cooling have been split capabilities, requiring different TEM holders. In-situ cryogenic cooling and biasing of specimens during scanning/transmission electron microscopy (S/TEM) has previously enabled the in-situ characterization of various quantum interfaces and chemical phase interactions in battery materials and other strongly correlated systems [1]. Quantum material responses must be studied under cryogenic conditions because many of the relevant properties in these materials only manifest below certain temperatures, while battery material interfaces are sensitive to electron beam damage when not cooled.

Combined in-situ sample heating with biasing has only become available in recent years with the use of the chip-based experimental platform, which has enabled capture of high-temperature microstructural and microchemical evolution alongside measurement of high-temperature electrical response in materials systems. Now, with the inclusion of on-chip biasing and thin film heater chip designs, we have developed a novel in-situ cryo-biasing heating TEM holder which enables simultaneous electrical stimulus and imaging of a sample across the full temperature range from cryogenic temperatures to over 1000°C , while matching room temperature (RT) microscope spec for resolution and drift. The basic functionalities of heating, cooling, biasing, and imaging are demonstrated alongside discussion of different applications.

Methods

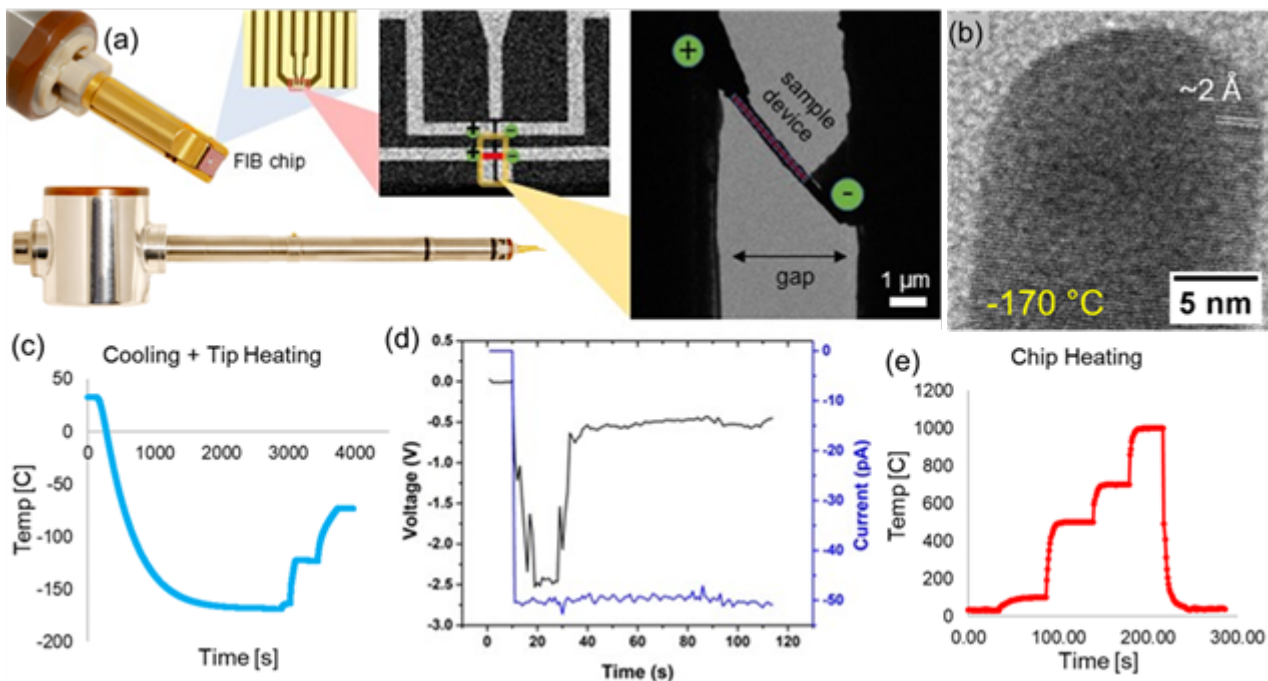
The TEM sample holder has an attached LN₂ dewar that cools the sample down from RT to the lowest operating temperature ($< -170^{\circ}\text{C}$) and can be controlled via software with closed-loop feedback at any temperature up to RT. Below RT where on-chip temperature measurements become increasingly inaccurate, precise temperature control is maintained using a conventional resistance heater and miniature thermocouple at the sample in the TEM holder tip. Nine electrical contacts to the user's sample or device allow on-chip biasing. Biasing experiments can now also be extended above RT to $>1000^{\circ}\text{C}$ using thin film sample heating with reliable on-chip temperature sensing. Since the heated area is small, the response time to temperature changes is fast and sample drift is minimized across the entire temperature range, resulting in image stability that matches the RT performance. Here, we present an example of a battery process after cooling a single nanowire system from RT down to liquid nitrogen temperature $\sim -170^{\circ}\text{C}$ [2].

Results

In Fig 1a, electrical biasing was performed on a nanowire sample bridging the electrodes on a biasing chip using this holder at RT down to near-liquid nitrogen temperature to protect damage in these beam-sensitive materials [2]. With constant current applied at cold temperatures, the voltage drops across the nanowire as a reaction proceeds with the plating of a dendrite layer on the surface, as shown in Fig 1d. In Fig 1b, atomic lattices are shown as a demonstration of resolution. Temperature control of the cooled and heated ranges is also shown in Fig 1c and 1e, respectively. The figures exhibit the core functionalities of the tool: stable and reliable sample biasing, heating, and cooling under atomic resolution TEM.

Conclusions

The In-situ cryo-biasing heating TEM sample holder presented here enables, for the first time, simultaneous electrical stimulus and high-resolution imaging of a sample across the full temperature range, from cryogenic up to high temperatures. This instrument will accelerate the development of the next generation of electronic, quantum, and energy storage materials devices. Combination of the two temperature regimes expands the range of temperatures available for dynamic temperature experiments, wherein multiple processing, imaging, or synthesis steps must be performed at various temperatures. High-resolution in-situ observation of operating (solid-state) battery interfaces in their full operational range of -40°C to 80°C is traditionally difficult to achieve due to air sensitivity, electron beam damage at RT, and lack of temperature control in TEM biasing platforms [3-5]. With this new tool, batteries may now be electrochemically cycled in situ at their entire operating range and then lowered to cryogenic temperature for imaging to combat electron beam effects, without the need for sample transfer between tools. With increasing demand for batteries that function at high temperatures, quantum material responses, synthesis, and processing, and material phase information from cryogenic to high temperature, the cryo-biasing TEM holder will provide the expanded versatility required of temperature-controlled in-situ electrical biasing systems.



Keywords:

cryogenic, heating, transmission electron microscopy

Reference:

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