6. Public Summary

The Zernike Insitute of Advanced Materials (ZIAM) is an internationally recognised, leading materials science institute, embedded in the Faculty of Science and Engineering (FSE). The institute's focus is to design, understand and control functional materials that are relevant to societal problems, by covering the full chain, from curiosity driven fundamental research, via synthesis and advanced characterisation, theoretical understanding and prediction, up to devices. The diverse group of 38 principle investigators and ~200 PhD students (total team size of 322 people – December 2022) is very diverse in multiple dimensions (e.g. age, gender, culture and experience) and ZIAM *uniquely* combines materials research expertises from physics, chemistry, biosciences and engineering within one institute, leading to groundbreaking discoveries.

The vision of ZIAM is to foster collaborative, multidisciplinary research, while respecting and stimulating the expertise and high quality of the individual groups. This leads to proven high-impact results and excellently trained (junior) researchers. Our mission is the design and scientific study of materials for functionality, comprising of four specific objectives; (i) to address fundamental and challenging questions in the fields of functional materials that are relevant to societal problems; (ii) to facilitate and encourage the transfer of knowledge and overall synergy of all disciplines relevant for materials research (physics, chemistry, biology, and engineering); (iii) to train new generations of researchers in cross-disciplinary approaches to research and to equip them with the diverse skills required by modern science; (iv) to maintain and strengthen our position as an internationally recognized, leading materials research and training institute.

In the coming period, we will pay special attention to the (changing) academic culture. That means supporting, embedding and career advancement of our large group of (tenure track) staff, and remain active in the national and European movement towards Recognition & Rewards, thereby fostering diversity in all dimensions as a strength and as such make use of the various talents that we have present. At the same time, we will take a lead in the development of programs to enhance social safety in the institute and faculty.

The scientific staff is working in one or more of the following (interconnected) research themes: Energy Materials, Quantum Materials, Sustainable Polymers, (Supra-)Molecular Assemblies, Advanced Instrumentation and Materials for Future Semiconductor Industry, and Cognitive Materials & Devices. The research is part of the FSE research theme 'Advanced Materials,' and we collaborate strongly with our sister institutes via the Zernike Institute National Research Center, the Groningen Engineering Center, CogniGron and HTRIC, and we are active member of the Aletta Jacobs School of Public Health, the Wubbo Ockels School of Energy and Climate, and the University of the North. In addition, we have multiple strategic regional, national and international collaborations and alliances, covering different ranges of knowledge institutes and types of industries. ZIAM PIs are leading or collaborate in large (inter)national networks and collaborations (academic and public private partnerships), a token of their scientific excellence and leadership. This has also led to large personal as well as collaborative funding, significant amounts also confirmed for the coming years (multiple ERCs, VICI, gravitation programs, NWA-ORC, National Growth Funds, etc.), demonstrating future viability. Moverover, ZIAM staff is well positioned in national and international boards, committees and advisory panels, and are as such part of setting future (science) policies and agendas.

The interdisciplinary team of ZIAM contributes to a large number of educational BSc and MSc programs of the faculty and university, i.e. physics, applied physics, chemistry, chemical engineering, biomedical engineering, industrial engineering & management, and life-science & technology. High profile Master programs in materials science, i.e. Top Master Nanoscience and High Tech Systems and Materials Honours program, have been developed by the institute, preparing students for cutting-edge interdisciplinary research in nanomaterials and interaction with industry respectively. The staff is very committed to all programs and prepare students for a career in (interdisciplinary) materials science.

Energy Materials: generating, saving and storing the energy of the future

A sustainable future requires radical changes in the way we generate, store and not waste energy. Such changes are impossible without novel materials, optimised specifically for energy applications: energy materials. That is why the ZIAM is very active in the fields of photovoltaics (generating electricity from sunlight), thermoelectrics (generating electricity from heat) and—more recently batteries (storing energy).

Materials for photovoltaics

Towards new photovoltaics, ZIAM pioneers a promising material class that is taking the solar cell world by storm: *metal halide perovskites*. Whereas the most widely studied and successful metal halide perovskites are based on lead, which is toxic, Protesescu's group showed how lead can be replaced by tin to yield stable 2D and 3D perovskite nanostructures [1], while Loi's group showed how to increase the conversion efficiency of solar cells using tin-based perovskites, a discovery that is now being followed up around the world [2]. This success in making high-quality perovskites also opens new avenues towards the holy grail of photovoltaic devices: the *hot-carrier solar cell*. Extracting charge carriers before they cool to the lattice temperature can lead to radically higher efficiencies than those of conventional solar cells. Loi's group discovered that hot carriers can have unusually long lifetimes tin-based perovskites [3], while Pchenitchnikov's group demonstrated that they can be extracted using organic electron transporters [4]. These insights are essential for the development of a new class of optoelectronics.

Another promising material class for solar cells is *organic materials*. We study promising organic semiconductors, from theory (Havenith, Marrink) via synthesis (Hummelen, Chiechi) to characterisation (Koster, Loi, Portale, Pchenitchnikov). ZIAM has a long and proud track record in the field of organic solar cells. In these devices, the exciton diffusion length is much shorter than in their non-organic counterparts, which puts severe constraints on the size of acceptor and donor domains. In collaboration with Anthopoulos' group, Koster's group quantified the exciton diffusion lengths in non-fullerene acceptors, which can range up to tens of nanometres [5], paving the way for the next generation of organic photovoltaics.

To guide the development of new materials, Koster's group also connected macroscopic performance indicators of solar cells to material properties [6]. The group's open-source *numerical modelling software package* has already quantified the unwanted losses in state-of-the-art perovskite solar cells [7], revealing that recombination at internal materials interfaces is the main source of losses. In another landmark paper [8], Koster's group also explained how to determine trap densities and charge-carrier mobilities in single-crystal perovskites [6].

Materials for thermoelectrics

Organic semiconductors also hold great promise for efficient thermoelectric generators, which directly convert (waste) heat into electrical energy. The challenge here is finding the n-type semiconductors required for such devices. Koster's group pioneered the use of ethylene glycol side-chains in organics as a means to improve their dielectric properties and doping efficiency. This resulted in a record performance in n-type organic thermoelectrics based on a single host [8]. What makes this a remarkable result is that it was achieved in the bulk, which is much more appealing than having to nanostructure thin films.

Materials for batteries

As part of the energy transition, battery technologies need to become more sustainable, and stationary energy storage are needed to support renewable energy sources or alleviate the electricity grid. Towards these ambitions, Tromp's group focuses on understanding the charging, discharging and deactivation mechanisms of batteries, using novel operando time- and spatially resolved characterisation techniques. By characterising the intermediates formed in electrodes and electrolyte separately, important insights in cycling and deactivation mechanisms for different battery types have been obtained. This, in turn, resulted in promising suggestions for novel battery materials and chemistries and cell improvements [9-11]. Much of this work is in direct collaboration with relevant companies scaling up and further.

FIGURE

The molecular packing of highly efficient n-type organic thermoelectrics: a,b) Grazing-incidence wideangle X-ray scattering (GIWAXS) patterns of pristine films and corresponding (c,d) linecuts. Panel e shows snapshots of molecular dynamics simulations that illustrate how the molecules pack, which is key to obtaining record thermoelectric performance. From [12].



Team

The PIs working within ZIAM's Energy Materials theme have been very visible. Next to excellent publications, they received multiple tokens of recognition, such as EU grants (ERC Advanced Grant for Loi, EU Horizon Europe grants for Loi and Koster) and NWO grants (Veni for Protesescu). ZIAM is part of the BatteryNL project (NWA-ORC, 9 M€, Tromp co-lead) that started in September 2022. Tromp was part of an expert group of the Ministry of Economic Affairs who wrote the 2022 Action Agenda for Batteries for the Netherlands and is figure head and board member of the Battery Competence Cluster NL. Very recently, large National Growth Funds have been awarded in the energy field with ZIAM involved and leading resp., i.e. SolarNL (Loi) and Materials Independence and Circular Batteries (Tromp).

- [1] Adv. Mater. 34, 2201353 (2022) https://onlinelibrary.wiley.com/doi/full/10.1002/adma.202201353
- [2] Advanced Energy Materials **8**, 1702019 (2018) <u>https://onlinelibrary.wiley.com/doi/full/10.1002/</u> aenm.201702019
- [3] Nature Comm. 9, 243 (2018) https://www.nature.com/articles/s41467-017-02684-w
- [4] Sci. Adv. 5 (11), eaax3620 (2019) https://doi.org/10.1126/sciadv.aax3620
- [5] Nature Comm. 11, 5220 (2020) https://www.nature.com/articles/s41467-020-19029-9
- [6] J. Open Source Softw. 7, 3727 (2022) https://joss.theoj.org/papers/10.21105/joss.03727
- [7] ACS Energy Lett. 2, 1214 (2017) https://pubs.acs.org/doi/10.1021/acsenergylett.7b00236
- [8] ACS Energy Lett. 6, 1087 (2021) https://pubs.acs.org/doi/10.1021/acsenergylett.0c02599
- [9] Nature Comm. 11, 5694 (2020) https://www.nature.com/articles/s41467-020-19537-8
- [10] J. Phys. Chem. C 122 (10), 5303 (2018) <u>https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.7b12799</u>
- [11] J. Electrochem. Soc. 165 (7), A1288 (2018) https://iopscience.iop.org/article/10.1149/2.0181807jes
- [12] J. Electrochem. Soc. 166 (2): A378 (2019) https://iopscience.iop.org/article/10.1149/2.1151902jes

Sustainable polymers: making plastics fit for the future

Plastic is at the same time an incredibly useful and versatile material, and an urgent challenge in terms of a sustainability future. ZIAM is leading the way in developing sustainable polymers that meet societal needs without causing harm to the environment, health, or economy. Building upon 55 years of leadership in polymer science at the University of Groningen, the institute develops new and innovative ways to make plastics fit for the future.

Green routes to produce plastics

The Loos group has been pioneering new and more sustainable ways to create biodegradable or recyclable plastics. Instead of applying conventional production methods to fossil fuels as raw material, renewable resources and the toolkit of biotechnology are exploited. The traditional way to catalyse the process of polymerization is by using metal-based catalysts that are often toxic: the Loos group has shown that enzymes, nature's own catalysts, can do the same job more efficiently, without using these harmful substances. They demonstrated that enzymatic polymerisations are perfectly suited for the design of complete green production routes using renewable resources, green solvents and molecular design principles for the circular economy. Loos is a trailblazer when using biotechnological approaches for producing those plastics that make up 35-40% of the entire plastic production worldwide. The group's many scientific breakthroughs in this context include:

- Novel biocatalytic synthesis routes towards poly(saccharide acrylates) [1,2], which are water-soluble, non-toxic, biocompatible and biobased. Whereas conventional synthesis routes are extremely complex and require many steps, this new biocatalytic pathway is fast, easy and non-toxic, and can be performed under safe conditions.
- The first fully enzymatic polymerisation route towards semi-aromatic polyamides [3] and poly(ester amides) [4].
- Fully green (i.e. bio-based) formulation of polyurethanes [5,6] and polyesters [7,8] etc..
- Green alternatives for polyethylene terephthalate (PET) [9]. Known for its large-scale use in plastic bottles, PET is typically produced from petroleum-based building blocks. Loos pioneered the use of biobased furan building blocks, polymerised using commercially available enzymes. The resulting "bio-PET" could very well revolutionise the world of plastics.
- A recyclable bioplastic membrane to clear oil spills from water [10], developed together with
 researchers from the Stenden University of Applied Sciences (NHL Stenden). This innovation won
 the KIJK magazine "best tech idea 2021" audience award and is part of the thesis that won the <u>Best
 Engineering Thesis Award</u> of the Groningen Engineering Center. Stenden and Groningen together
 form the <u>Hybrid research group Biopolymer and Recycling Innovations (HyBRit)</u>, a key project of the
 University of the North. The HyBRit team was awarded the <u>NWO Team Science Award</u> in 2022.



Integral approach

By prioritising sustainability as well as functionality and performance in the development of new and familiar plastics, the institute is setting a new standard for environmentally responsible material development. The novel plastics developed at ZIAM are finding application in food, foams, and films (poly-saccharides), cosmetics (glycopolymers), fibres (polyester, polyamides) and bottles (polyester, biobased PET alternatives). In her research, Loos considers the entire life cycle of plastics – starting with biobased, renewable materials, limiting material and energy waste during production, reducing the CO2 footprint, and ensuring that the final products can be recycled or degraded biologically. This integral approach is set to make the plastics industry greener, and provide solutions to the growing issue of plastic pollution.

Team

Worldwide, Loos is among the most cited researchers in her field (last 10 years, SciVal). She initialised 16 public-private consortia in the last 10 years, involving almost all Dutch universities active in the area and about 30 companies. NWO awarded two of these consortia a total of 6 M€. Alongside, the Zernike polymer science team has grown considerable through the hires of Giuseppe Portale (Polymer Physics, 2015), Marleen Kamperman (Polymer Science, 2018) and Dina Maniar (Polymer Composites, educational tenure track, 2022). Their complementary expertise offers not only strong collaborative opportunities within the institute but also links to different other research fields such as energy materials, health, and engineering.

- [1] Green Chemistry. 20 (2), 476-484 (2018) <u>https://doi.org/10.1039/C7GC03023A</u>
- [2] Carbohydrate Polymers. 193, 196-204 (2018) https://doi.org/10.1016/j.carbpol.2018.03.098
- [3] RSC Advances. 6 (72), 67941-67953 (2016) <u>https://doi.org/10.1039/C6RA14585J</u>
- [4] Polymer. 205, 122662 (2020) <u>https://doi.org/10.1016/j.polymer.2020.122662</u>
- [5] ACS Omega. 5 (3), 1488-1495 (2020) <u>https://doi.org/10.1021/acsomega.9b03203</u>
- [6] Journal of Applied Polymer Science. 136 (20), 47454 (2019) https://doi.org/10.1002/app.47454
- [7] ACS Polymers Au. **3** (1), 82–95 (2022) <u>https://doi.org/10.1021/acspolymersau.2c00035</u>
- [8] ACS Sustainable Chemistry & Engineering. 8 (2), 1068-1086 (2020) <u>https://doi.org/10.1021/acssuschemeng.9b05874</u>
- [9] ChemSusChem. 12 (5), 990-999 (2019) <u>https://doi.org/10.1002/cssc.201802867</u>
- [10] Advanced Materials. 33 (15), 2008460 (2021) https://doi.org/10.1002/adma.202008460

CogniGron: electronics taking inspiration from the brain

When today's transistors reach their miniaturisation limits, what devices will take over their role? To answer this question, ZIAM joined forces with the neighbouring Bernoulli Institute for Mathematics, Computer Science and AI to establish the Cognitive systems and Materials Center (CogniGron). CogniGron aims to reduce the energy consumption of computing devices. This is urgently needed for the sustainable future of AI and data processing, and expected to transform a range of technologies, from sensors (edge computing) to data centres (cloud computing). CogniGron pioneers a new generation of neuromorphic or cognitive computing, which takes inspiration from the way the brain handles huge amounts of data using minimal amounts of energy. The centre performs fundamental research but also creates demonstrators to study and showcase the potential of their approach.

Revolutionary ferroelectrics

A prominent example concerns hafnia-based ferroelectrics, which are revolutionising the field due to their CMOS compatibility and unprecedented nanoscale stability. With others at the institute, Noheda's group discovered a novel phase in $H_{0.5}Zr_{0.5}O_2$ [1] and combined epitaxial material growth with the most advanced *in-operando* electron microscopy [2] to reveal the interplay between ferroelectric switching and ion (oxygen vacancy) migration across the $La_{0.67}Sr_{0.33}MnO_3 / Hf_{0.5}Zr_{0.5}O_2$ layers [3] (see Figure 1). The interplay between ionic and electronic transport at the nanoscale gives rise to memristive behaviour, meaning that the material can retain a state of internal resistance based on the history of applied voltage and current.

Memristors

Memristive devices have gained great attention due to their potential for brain-inspired computing and perception. The conductance of a memristor can be modulated by a voltage pulse, which is crucial for the building blocks for artificial neural networks. Banerjee's group used interface memristors made from Nb-doped SrTiO₃ to show that in the right sequence, a train of voltage pulses can encode information, which can be read out by applying a small voltage signal [4]. Chicca's group, working with the Engineering Institute (ENTEG), coupled piezoresistive sensors made from carbon nanofibres and plastic with neural networks to mimic skin-like sensing. This allowed them to create a bio-inspired gesture-tracking smart glove [5].

Piezoelectric tiles

The demonstrators not only serve scientific discovery, they are also eminently suited to engage with society and tell the story of the future of electronics. Together with the ENTEG Institute, Science-LinXs (the outreach organisation of the university) and the neighbouring townhall Zuidhorn (Gemeente Westerkwartier), CogniGron researchers developed a demonstrator of a piezoelectric tile, which was <u>installed</u> at the bus stop in Zuidhorn. The electrical signals generated upon stepping on the tile are collected and visualized on a server that allows analysing the passenger flows and behaviour. The modular system allows to replace the piezoelectric of the tile (as the materials keep improving) as well as the electronics (once digital chips will be substituted by increasingly efficient neuromorphic chips). Information panels on-site inform the pedestrians about piezoelectric and other forms of energy harvesting and about brain-inspired computing, as a way to keep the people in the street connected with the research performed at the university. With this project, CogniGron is also part of NL-ECO, a new programme of the Dutch National Science Agenda (NWA) that works together with other Dutch partners interested in developing novel energy-efficient computing platforms.

Team

The types of materials, devices, architectures and software required for the future of energy-efficient electronics, are substantially different from those in today's digital computers and their design requires a stronger synergy between the different disciplines. With a multidisciplinarity that has been called a "pioneering example", the CogniGron groups aim to educate a new generation of scientists. This is possible thanks to a generous private donation, unprecedented in Dutch academia, funding 30 PhD multidisciplinary projects over the span of 7 years and 12 new professors, including 2 at ZIAM, with the expertise needed to venture into brain-inspired electronics.

FIGURE 1

In-operando scanning tunneling electron microscopy (STEM) experiments on hafnia-based ferroelectric memristive devices. The $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) bottom electrode reversibly transforms from the perovskite (P) phase (a) to the brownmilletate (B) phase (b) upon electrical cycling from -3V to +3V. The P-to-B phase transition releases oxygen ions into the $Hf_{0.5}Zr_{0.5}O_2$ layer, while the B-to-P transition generates oxygen vacancies (V_o). By means of integrated phase-difference contrast (iDPC)-STEM, V_o can be followed across the $Hf_{0.5}Zr_{0.5}O_2$ layer up to the top electrode, as the the electric field applied in-situ to the device is increased (c). The iDPC-STEM images taken at 0 V, 1 V and to 2 V are shown in d)-e), respectively.



- [1] Nat. Mater. 17 (12), 1095 (2018) https://pubmed.ncbi.nlm.nih.gov/30349031/
- [2] Sci. Adv. 6, eaay4312 (2020) https://www.science.org/doi/10.1126/sciadv.aay4312
- [3] Science 372 (6542), 630 (2020) https://www.science.org/doi/10.1126/science.abf3789
- [4] Appl. Phys. Lett. 122, 034101 (2023) <u>https://doi.org/10.1063/5.0124135</u>
- [5] ACS Appl. Elec. Mater. 4 (1), 308 (2022) https://pubs.acs.org/doi/10.1021/acsaelm.1c01010

Quantum materials: quantum phenomena for new functionalities

In quantum materials, the laws of quantum mechanics result in unique material and device behaviours for applications ranging from (quantum) computing, communication and sensing, to (green) energy. ZIAM aims to accelerate the development of novel quantum materials and devices using state-of-theart nanofabrication and nanocharacterisation techniques. Exploiting our strong track record in the theory and fabrication of new quantum materials, heterostructures and devices, we turn collective quantum phenomena into new functionalities.

In two dimensions...

Since the discovery that graphene, a single layer of carbon atoms organised in a hexagonal lattice, can be obtained from exfoliating a graphite crystal, a new research field evolved into the physical phenomena in two-dimensional (2D) materials. Stacking these materials onto each other via van der Waals forces opens the possibility of creating heterostructures, and combining their electronic, magnetic and optical properties. For example, the van Wees group investigates various forms of spintronic and magnetic proximity effects in such van der Waals systems. They combined the excellent spin and charge transport properties of graphene, adding 2D materials with large spin-orbit interactions, such as transition metal dichalcogenides, to create new classes of magnetic/spintronic devices [1]. Recently the group discovered that graphene, when combined in a van der Waals heterostructure with an antiferromagnetic insulator, becomes magnetic itself [2] (Fig. 1).

FIGURE 1.

Schematic picture of a van der Waals heterostructure of (bilayer) graphene and a layered antiferromagnet CrSBr. As a result of the magnetic proximity effect, the graphene has become effectively magnetic [2].



The Ye group focuses on the unique superconducting properties of 2D materials [3]. Due to the Ising-like spin structure of transition metal dichalcogenides, their superconductivity was found to be very robust against large magnetic fields [4]. By combining this unusual spin-dependent band structure with high-quality devices made from 2D materials, the group could demonstrate new phases of super-conductivity. The group of Guimaraes investigates the link between optoelectronics and spintronics in 2D materials [5]. They demonstrated new and unique manifestations of spin-orbit torques and interactions with ferromagnets, depending on the specific crystal orientation and symmetry of the materials. These effects enable more efficient switching of the magnetisation by electrical currents, thus paving the way for new types of magnetic memories [6]. In addition to spin transport carried by electrons, the van Wees group demonstrated that magnons, the elementary magnetic excitations in ferromagnets, can also be very efficient spin transporters, even in very thin insulating materials [7]. They also succeeded in observing and even controlling this transport in 2D (anti) ferromagnet materials [8,9]. Finally, the new theory group of Slawinska categorised the various classes of quantum materials which can provide unusual conversion between spin and charge currents [10]. In collaboration with the van Wees group, they are studying the unique spin charge conversion by WTe₂.

...and beyond

In further work on quantum materials, the van der Wal group investigated new types of defects in SiC which can host spin-based quantum bit ("qubit") systems, and provide an alternative to the NV centre defects in diamond currently used for quantum information processing and communication [11]. And finally, in recent years, the van der Wal and van Wees groups made a connection between the manifes-

tation of chirality in molecular and solid-state systems and various physical phenomena, including chirality-induced spin selectivity, which is the key to the spintronics of the future [12]. The results triggered several interdisciplinary collaborations between ZIAM and other institutes.

Team

Research into quantum materials has been supported by ERC grants (Advanced Grant for van Wees, 2020; Starting Grant for Guimaraes, 2021), NWO grants (Gravitation grant "Quantum Materials", 2022; XL grant "The two-dimensional magnon gas in atomically thin magnets") and the National Growth Fund ("Quantum Delta NL", 13 M€). Spinoza Laureate (2016) Bart van Wees is the figurehead of the quantum material activities at the Zernike Institute and his leading role in the field has been appreciated by e.g. leading the Spintronics work package within the EU Graphene Flagship. The research in quantum materials has been recently strengthened by new hires (Antonija Grubisic-Cabo, surface science; Roberto Lo Conte, scanning tunnelling microscopy of 2D materials).

- [1] Nano Lett. **19** (9), 5959 (2019) <u>https://pubs.acs.org/doi/10.1021/acs.nanolett.9b01611</u>
- [2] Nature Nanotechn. 16, 788 (2021) https://www.nature.com/articles/s41565-021-00887-3
- [3] Nature 556, 43 (2018) https://www.nature.com/articles/nature26160
- [4] Nature (2023) https://www.nature.com/articles/s41586-023-05967-z
- [5] Phys. Rev. B 103, 115410 (2021) https://journals.aps.org/prb/abstract/10.1103/PhysRevB.103.115410
- [6] arXiv:2303.03892 (2023) https://arxiv.org/abs/2303.03892
- [7] Nature Materials 21, 1352 (2022) https://www.nature.com/articles/s41563-022-01369-0
- [8] Phys Rev B 101, 205407 (2020) <u>https://journals.aps.org/prb/abstract/10.1103/PhysRevB.101.205407</u>
- [9] Phys. Rev. B **107**, L180403 (2023) <u>https://journals.aps.org/prb/abstract/10.1103/PhysRevB.107</u>. L180403
- [10] Phys. Rev. Materials 6, 045004 (2022) https://journals.aps.org/prmaterials/abstract/10.1103/PhysRevMaterials.6.045004
 [11] Appl. Phys. 121 (0) 004401 (2022)
- [11] J. Appl. Phys. 131 (9), 094401 (2022) https://pubs.aip.org/aip/jap/article/131/9/094401/2836587/Electromagnetically-inducedtransparency-in
- [12] Nano Lett. 20 (8), 6148 (2020) https://pubs.acs.org/doi/10.1021/acs.nanolett.0c02417

EUV: Advanced instrumentation and materials for the microchips of the future

State-of-the-art lithography tools have made the revolutionary, bold switch from UV light to extreme ultraviolet light (EUV) with a wavelength of 13.5 nm. This enables the production of ever smaller and faster devices, which is crucial for the semiconductor industry to keep pace with Moore's law of doubling the number of devices on a chip every two years. The EUV light is created by highly charged tin ions in hot laser-driven plasmas. Making sure that these plasmas of increasing power can be safely contained while harvesting the precious EUV light is one of the topics addressed in the Quantum interactions and Structural Dynamics groups of Hoekstra, Schlathölter and Bari.

Radiation and debris

Keeping up with Moore's law requires pushing EUV sources to ever higher powers, which challenges the plasma-facing equipment, especially the complex multilayer Mo/Si reflectors. Studying the plasma output, the group showed that in particular the first mirror collecting the EUV light is also exposed to out-of-band radiation [1,2] and plasma "debris" comprising, e.g., tin clusters, fast tin ions [3,4], or ions accelerated to its surface by the plasma sheath, which might damage the optics. As H_2 gas has the lowest absorption of 13.5-nm light, a large flow of H_2 buffer gas is used to mitigate entrainable debris. The group currently try to understand when this debris indeed becomes entrainable in the gas flow, and if the H_2 mitigation strategy will be sufficient when scaling to higher source powers, or for EUV sources in which present-day CO_2 lasers are replaced by power-efficient solid-state lasers to drive the plasma, generating tin ions of even higher energy [5,6].

FIGURE 1:

ZERNIKELEIF is a unique low-energy ion beam facility where (multiply) charged tin ion beams can be produced that are selected on energy, charge state, and mass. The resulting ion beams serve two experimental setups, one to study the interaction of tin ions with gasses, and one to study ion interactions on surfaces.



Ion beam experiments

The group's low-energy ion beam facility ZERNIKELEIF (Fig. 1) with its advanced auxiliary equipment is a worldwide unique facility to investigate the interaction of highly charged ions with gasses and solids. It has recently been modified to specifically address EUV source-related questions, such as how heavy tin ions get entrained in a gas of light molecules, how this depends on the charge state of the ions, and what the sputtering and implantation rate is of tin ions on clean and debris-covered surfaces. Experiments are called for as all available models are inadequate in their description. This is evident from the group's first experiments on electron capture by Sn³⁺ ions on H₂ and D₂[7], see Fig. 2. The data cannot be reproduced by the most advanced semi-quantal calculations (orange curve), indicating that the Frank-Condon approximation breaks down and full quantal calculations must be developed. We have secured the funds to install a reaction microscope so that our experiments will be able to collect state-to-state information as well.

FIGURE 2

Comparison of experimental data with different semiclassical calculations of single electron capture cross sections in Sn^{3+} collision with H_2 (black symbols) and D_2 (red symbols) as a function of the ion energy.



Team

The EUV research is embedded in the Advanced Research Center for Nanolithography (ARCNL). This collaboration started as a public-private partnership between the University of Amsterdam, the Vrije Universiteit Amsterdam, the Dutch Research Council (NWO) and the semiconductor equipment manufacturer ASML. On 1 January 2022, the University of Groningen joined as associate partner. Ronnie Hoekstra is one of the founding fathers of ARCNL and group lead at ARCNL since its start in 2014. The ZIAM team has been widening its research portfolio: EUV interactions with molecules in the direction of EUV photoresists are now pursued by Thomas Schlathölter and by Sadia Bari of DESY Hamburg, who has been appointed to honorary professor and joined the QISD group in 2022. On the materials side, collaborations are being established within ZIAM on advanced instrumentation such as GISAXS (Portale group) and TEM (Kooi group) to characterise advanced materials for use in EUV lithography machines [8].

- [1] JPB 51, 045001 (2017) https://iopscience.iop.org/article/10.1088/1361-6595/aab533
- [2] AIP Adv. 11, 125003 (2021) https://doi.org/10.1063/5.0073839
- [3] Phys. Plasmas 29, 123102 (2022) https://doi.org/10.1063/5.0129112
- [4] Plasma Sources Sci. Technol. 30, 105006 (2021) <u>https://iopscience.iop.org/article/10.1088/</u> <u>1361-6595/ac2224/meta</u>
- [5] Phys. Rev. Res. 3, 013294 (2021) <u>https://journals.aps.org/prresearch/abstract/10.1103/PhysRev</u> <u>Research.3.013294</u>
- [6] J. of Opt. 24, 054014 (2022) https://iopscience.iop.org/article/10.1088/2040-8986/ac5a7e/meta
- [7] Phys. Rev. A 106, 12804 (2022) https://journals.aps.org/pra/abstract/10.1103/PhysRevA.106.012804
- [8] Phys. Rev. Mat. 6, 043402 (2022) <u>https://journals.aps.org/prmaterials/abstract/10.1103/</u> PhysRevMaterials.6.043402

Supramolecular assemblies: exploring and exploiting nature's unique assembly pathways.

Supramolecular assemblies are collections of (bio)molecules held together by non-covalent interactions. They play an important role in biology, but are also at the basis of novel advanced materials with adaptive, life-like properties. The molecular and physical rules that control self-assembly are complex and only partly understood. ZIAM researchers follow a multidisciplinary approach to elucidate and control the formation and function of supramolecular assemblies, enabled by a wide range of complementary techniques including optical tweezers, high-speed AFM, super-resolution microscopy, optical molecular imaging, solid-state NMR, infrared spectroscopy, X-ray scattering (SAXS/WAXS), synthesis & rheology and molecular dynamics.

New light on supramolecular assembly pathways

Supramolecular assembly plays a central role in biology, underpinning the formation and function of key cellular protein complexes. Three highlights exemplify how ZIAM researchers shed new light on supramolecular assembly pathways with unprecedented spatial and temporal resolution, knowledge that can be efficiently translated into the rational design of novel bio-based materials and devices.

First, by combining high-speed AFM with optical tweezers, the Roos group was able to track the assembly process of the Hepatitis B virus (HBV) at single-molecule resolution. The results yielded a contact-rich pentameric arrangement of HBV proteins (see Fig. 1a) [1], which is not only relevant for HBV and other viruses, but also for new antiviral strategies.

Second, the Onck group studies the nuclear pore complex (NPC), an intriguing protein complex consisting of a large phase-separated assembly of intrinsically disordered proteins (IDPs) that facilitates nuclear transport (see Fig. 1b). By using residue-scale molecular dynamics techniques, they resolved the physical mechanisms that drive IDP phase separation and selective transport [2,3].

Third, phase separation and self-assembly of IDPs is also at the base of neurodegenerative diseases, including ALS and Huntington's disease. The van der Wel group used solid-state NMR (Fig. 1c) [4, 5] to resolve the polymorphic fibrillar structures of toxic amyloid fibres and how anti-amyloidogenic chaperones might prevent this. Mimicking how nature exploits phase separation and self-assembly enabled the Kamperman and Portale groups to synthesise biobased materials and devices with novel, adaptive properties, such as underwater adhesives [6] and conducting membranes and fibres [7]. The groups used e.g. rationally designed spider silk-inspired proteins (Fig. 1d) for proton conducting device fabrication.

FIGURE 1

Supramolecular assemblies studied by (a) high-speed AFM [1,8], (b) molecular dynamics [2,3], (c) solid-state NMR [5], (d) rational synthetic design [7].



Grants and outreach

The success, viability and multidisciplinary nature of these activities is reflected in more than 15 collaborative research grants in the last five years, typically ranging from 0.5 to 3 M€ per grant, and personal grants such as an ERC Consolidator Grant (Kamperman). Work on (supra-)molecular assemblies is intertwined with two Zernike-funded BIS consortia: (1) <u>Out-of-equilibrium chemical systems: exploiting</u> the fundamental principles of life and (2) Physics of cancer: cancer as a materials science problem. Lorentz Workshops on "<u>Out-of-Equilibrium Systems, Emergence, and Life</u>" and "<u>Cancer in a Physical Context</u>" were organised to connect to groups at the national level. The societal value of this work has received support from disease-specific foundations and industry. The results have been covered by media such as the HDBuzz website, a monthly column in the Dutch national newspaper *De Volkskrant, Faces of Science* blogs, television and radio (e.g. "Eva zoekt het uit", 2022), public lectures (e.g. at pop venue Paradiso, cultural festival Oerol, "Kinderuniversiteit" for 100 primary school children, "Scientist in the Classroom" lectures), a comic and lecture programme for elementary schools, a MOOC for high-school students and numerous public events. For her contributions to societal outreach, Kamperman was awarded the <u>Van</u> <u>Marum Medal</u> and the Pilot Fund 'Science Communication by Scientists: Appreciated!' (KNAW).

- [1] Sci. Adv. 7 (45), eabg0811 (2021) https://doi.org/10.1126/sciadv.abg0811
- [2] Nature Comm. 12, 2010 (2021) https://doi.org/10.1038/s41467-021-22293-y
- [3] PNAS 120 (25), e2221804120 (2023) https://doi.org/10.1073/pnas.2221804120
- [4] Nature Comm. 8, 15462 (2017) https://doi.org/10.1038/ncomms15462
- [5] Nature Comm. 12 (1), 946 (2021) https://doi.org/10.1038/s41467-021-21147-x
- [6] Adv. Mat. 1808179 (2019). https://onlinelibrary.wiley.com/doi/ full/10.1002/adma.201808179
- [7] Sci. Adv. 6 (29), eabc0810 (2020) https://doi.org/10.1126/sciadv.abc0810
- [8] JACS 142 (32), 13709 (2020) <u>https://doi.org/10.1021/jacs.0c02635</u>