RUHR-UNIVERSITÄT BOCHUM

RUB

MATERIALS RESEARCH DEPARTMENT

FOCUS ON:

↗ Microsystems Technology

NO. 18

Materials Research Department

MRD
MATERIALS RESEARCH
DEPARTMENT

FOCUS ON:
MICROSYSTEMS TECHNOLOGY:
FROM FUNDAMENTALS TO DEVICES

Microsystems technology is key for next-generation components and indispensable for integrating fundamental materials innovation into smaller, faster and more efficient devices.

The 18th MRD newsletter highlights research of the MRD in the area of microsystems technology. Like all previous newsletters, this issue is also accessible through the MRD website at www.mrd.rub.de.

We are looking forward to receiving feedback on the newsletter and welcome suggestions for the next issues.

Enjoy reading,

Ralf Drautz and Tong Li
MRD Speakers
Anastasiia Petrova and Denisa Voicu
MRD Science Managers

CONTENT

On the cover: Five chamber cluster-tool installed within the cleanroom of the ForLab Bochum.
© RUB, ForLab PICT2DES /André Wirsig

TRANSFORMATION OF MOLECULES TO ADVANCED FUNCTIONAL MATERIALS

A gateway to tune device functionalities

The development of nanostructured advanced functional materials on a scalable level bridging the worlds of nanoscale materials chemistry and device manufacturing is a promising strategy to tackle the challenges posed by emerging technologies in the field of micro/nano/optoelectronics, energy conversion, storage, optics, photovoltaics etc. The increasing demand to process new and sustainable materials and device systems can be addressed with an interdisciplinary approach including synthetic organic/inorganic chemistry, scalable materials synthesis, advanced material characterization and testing them for prototype device applications. Atomic layer processing (ALP) of functional materials via bottom-up processes that include chemical vapor deposition (CVD), atomic layer deposition (ALD), molecular layer deposition (MLD) and area selective deposition (ASD) are the front runners in terms of scaling up and nanostructuring of advanced materials for future emerging technologies.

The Inorganic Materials Chemistry (IMC) research group at RUB addresses the demand for new functional materials for advanced applications such as nano/microelectronics, photovoltaics, energy-related technologies etc. by transforming molecules (precursors) to functional materials employing chemical gas phase deposition methods. Predominantly the mate-

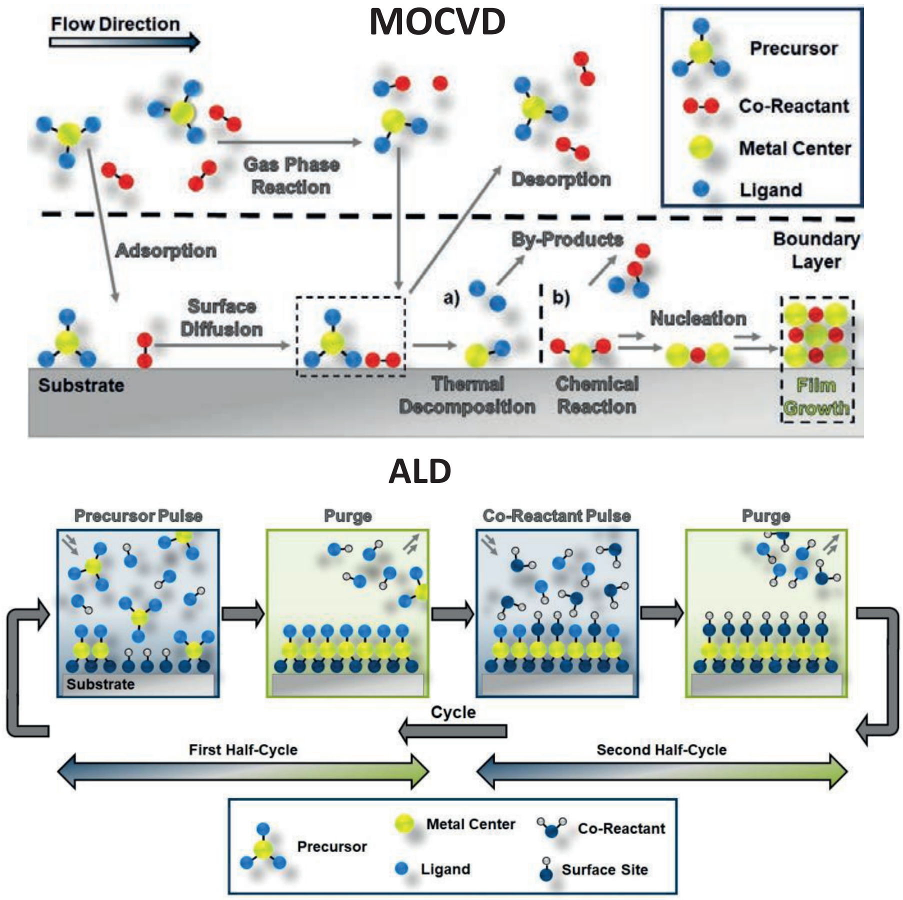


Figure 1: Schematic of MOCVD (top) and ALD (bottom) processing of materials.

rials synthesis is achieved by MOCVD and ALD (Figure 1). These methods enable thin film deposition on large areas with very good control of thickness and conformal coverage on complex device geometries. Several types of substrates (wafers, flexible foils, high aspect ratio structures) of varying sizes and shapes can be coated. The precursors employed have an important bearing on the resulting film quality and properties. The research strategy employed by the IMC group involves a complete chain of workflows starting from the development of novel precursors, utilizing them for nanostructured thin film deposition and finally evaluating them for device applications as depicted in Figure 2.

By varying the process parameters such as substrate temperature and precursors employed, the properties of the materials are modulated to suit the demands of the devices under consideration. Particularly, ALD has become a very important technology for depositing very thin layers of a few nanometer thicknesses. ALD processing technology offers a large material variety, fostered by the inorganic chemistry delivering precursors, and driven by applications in several areas: microelectronics (gate stacks for scaled MOS transistors, programable resistive layers for resistive memories), optoelectronics, microsystems (optical or gas sensors), surface modifications (e.g., bio-compatible and bio-stable passivation layers for implants), for energy storage and conversion (batteries, catalysts), 2D membranes for gas separation to name a few. These are some of the research areas that the IMC group pursues within the scope of third party-funded projects. A wide range of material systems are investigated for various applications such as metals (e.g. Cu, Ag, Mo, Ru, Ir, Co, Al), metal oxides (e.g. ZnO, Al_2O_3, TiO_2, Y_2O_3, Gd_2O_3, WO_3, SnO_2, In_2O_3, Ga_2O_3), metal nitrides (ZrN, AlN, GaN, InN, TaN, TiN, GdN, DyN), metal sulfides (WS_2, MoS_2, HfS_2, SnS_2), hybrid materials of Cu, Al, Zn with organic reactants, multi-component systems ($CoFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$, $HfGdO_x$) etc.

The research in the IMC group focuses on the rational development of precursors for a range of elements and evaluating them using spectroscopic methods namely nuclear magnetic resonance (NMR), mass spectrometry (MS), infrared spectroscopy (IR) and the composition by elemental analysis (EA) and atomic absorption spectroscopy (AAS). The thermal properties which form an important figure of merit to qualify a precursor for CVD/ALD methods are investigated in detail to determine the evaporation/decomposition behavior and the vapor pressure. In addition, theoretical studies (done in collaboration) are performed to investigate the reactivity of the precursors towards different co-re-

Prof. Dr. Dr. (h.c.) Anjana Devi
Inorganic Materials Chemistry, RUB and Nanostructured Sensor Materials Group, Fraunhofer IMS, Duisburg

Dr. Harish Parala
Inorganic Materials Chemistry
harish.parala@rub.de

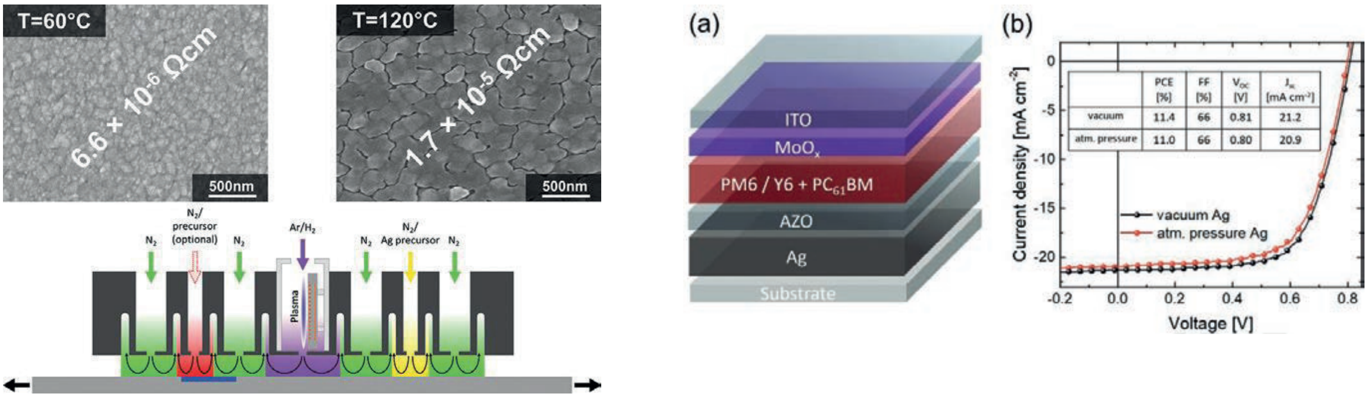


Figure 3: SEM images of percolated and conducting Ag films grown from carbene-based Ag(I) precursor (left). Layer sequence of the organic solar cell and current density versus voltage characteristics of top-illuminated organic solar cells based on APP-ALD (right), [3, 4].

actants (H_2, O_2, H_2O, H_2S, sulfur, NH_3) that gives insights into the suitability of the precursor for thin film deposition via MOCVD and ALD [1]. This includes density functional theory (DFT) and molecular dynamics (MD) simulations. The most promising precursors are scaled up and used for thin film growth via MOCVD), ALD and plasma ALD (PEALD). The deposited materials on various substrates (Si, glass, sapphire, polymers, TiN, glassy carbon etc.) are characterized using advanced materials characterization techniques that include X-ray diffraction (XRD), grazing incidence XRD (GI-XRD), X-ray reflectometry (XRR), scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), atom probe tomography (APT), time of flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), ellipsometry, contact angle and resistivity measurements, UV-Vis and Raman spectroscopy. The materials are then integrated in device structures for proof-of-concept demonstrators, done in collaboration with electronic engineers. Herein, two representative examples of some recent developments in the IMC group are highlighted.

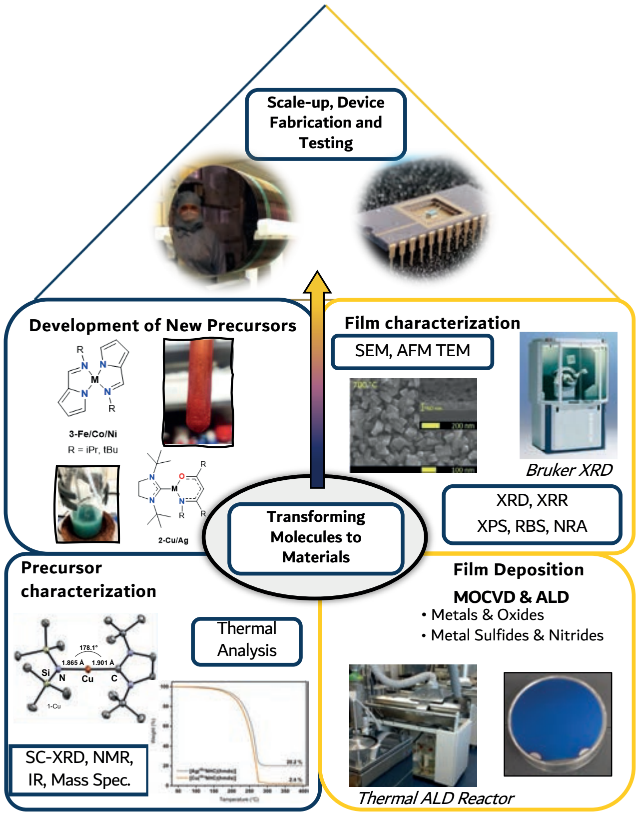
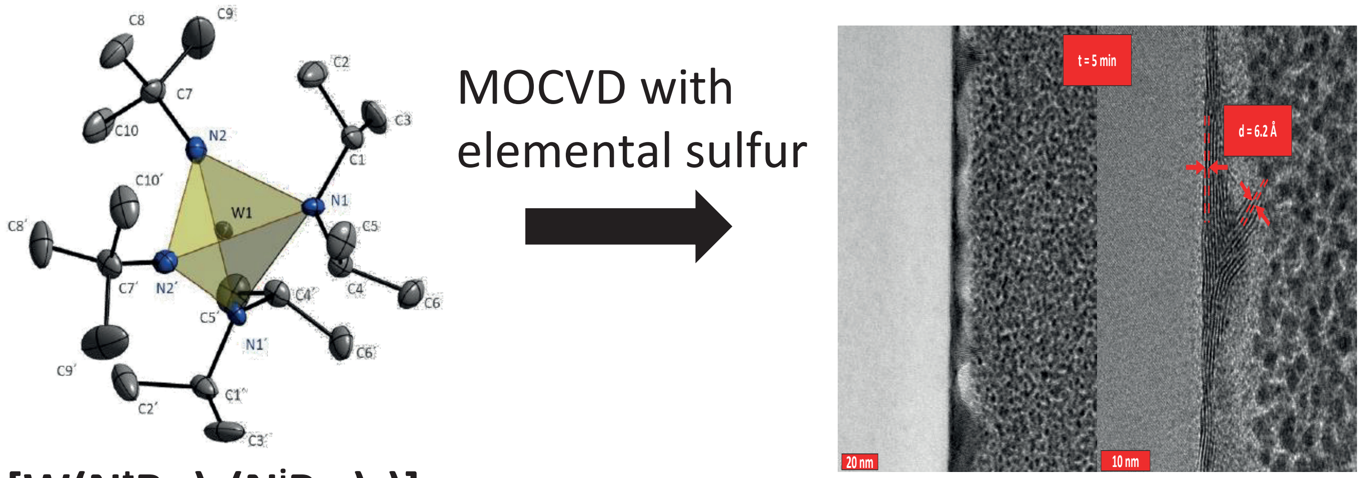


Figure 2: Research focus of IMC group @ RUB: From precursor chemistry to material synthesis, characterisation and device fabrication.

(a) Metal ALD: Although ALD has been well established for several metal oxides and a wide range of processes are already implemented for manufacturing in the industry, ALD of metals is still a challenge, especially for very thin metal layers where the nucleation and controlled growth is difficult to achieve. Hence, there is a huge interest in developing new metal precursors that can influence nucleation. One of the hurdles is the choice of co-reactants to reduce the precursor for metal film formation. Our recent approach in using alternative reducing agents for Co thin films for thermal ALD is very encouraging. New precursor combinations resulted in the growth of thin cobalt metal films with low resistivities [2]. In another case study, the identification of new carbene-based Ag precursors enabled the growth of conducting and percolated Ag thin films via spatial ALD (S-ALD) that were implemented successfully as bottom electrodes in solar cells (Figure 3) [3,4] demonstrating promising features. This work was done in collaboration with the group of Prof. Riedl (Bergische University of Wuppertal). Another



$[W(N^tBu)_2(N^iPr_2)_2)]$

Figure 4: A new tungsten precursor $[W(N^tBu)_2(N^iPr_2)_2)]$ successfully employed for WS_2 film growth via MOCVD using elemental sulfur as co-reactant (left). HRTEM image of few layers WS_2 grown on Si (right), [6, 7].

example is the deposition of Ru thin films as interconnect materials. A new class of Ru precursors were successfully used for Ru thin film deposition via MOCVD [5]. This work was done in collaboration with the industry collaborator, Heraeus AG. All these new developments in the field of metal ALD/CVD are highly encouraging and are a motivation for the scientific community to explore new precursors for challenging metals such as Cu, Ag, Ru, Mo, Co, Al etc.

(b) Two-dimensional (2D) materials: The enormous focus in the field of 2D materials, particularly on transition metal dichalcogenides (TMDC) such as MoS_2, and WS_2 is triggered by the interest in implementing 2D materials in future technological applications. Device platforms based on TMDC materials can offer overarching opportunities for next-generation electronics, optics, sensing and energy-related technologies. However, for their implementation, thin TMDC layers should be fabricated with a controlled thickness (mono to few layers) on large and complex substrates, which has so far been a challenge. The IMC group adopts an interdisciplinary approach by growing 2D materials using new precursor combinations via MOCVD and ALD. Figure 4 depicts the growth of a few WS_2 layers grown by MOCVD on Si substrates using a new tungsten precursor in combination with elemental sulfur leading to high-quality films. The WS_2 layers were implemented in proof-of-concept gas sensors and catalysts for hydrogen evolution reaction (HER) [6,7]. In collaboration with Fraunhofer Institute for Microelectronics Circuits and Systems (IMS) Duisburg, large area deposition of TMDCs (MoS_2) on 200 mm Si and USG wafers were achieved and successfully integrated as sensor elements [8].

In summary, new and improved metalorganic precursors form a gateway to fabricate new materials and devices via atomic layer processing routes. There is a huge potential to pursue this research strategy of transforming molecules into materials. The research carried out in the IMC group bridges both fundamental and applied research. This has led to strong collaboration and networking with leading research institutes and industry partners both at the national and international levels. RUB and IMS have established a strong interdisciplinary collaboration over the last years within the framework of research projects funded by EFRE (FunALD) and BMBF (FlexTMDSense). The Nanostructured Sensor Materials (NSM) research group at Fraunhofer IMS Duisburg has a joint cooperation agreement with RUB. Anjana Devi bridges the fundamental research done at RUB with the application oriented research towards device demonstrators at IMS. The ALD processes developed at RUB are scaled up on large wafers (200 mm) and integrated into the CMOS structures at IMS for device fabrication. Similarly, the precursors (for 2D materials and high-k oxides) developed in the IMC group are scaled up and implemented in the cluster tool of “Research Laboratory Microelectronics Bochum for 2D Electronics” (ForLab-PICT2DES project funded by the BMBF; the author Anjana Devi is one of the PIs in the ForLab consortium). The research work of the IMC group involves collaborative activities with leading scientists, research institutions and industries within the ALD and CVD communities spread out at the national and international levels. The projects have been supported by the generous funding from the DFG (individual grants, SPP and SFB projects, DFG-ANR), EU, DAAD, BMBF, Fraunhofer Society and Industry. The funding of the various projects and the past and present co-workers at IMC, IMS and collaborators are gratefully acknowledged.

REFERENCES:

1 Beer S. M. J., et al., Chemistry of Materials (2022), 34, 152.
2 Zanders D., et al., Chemistry of Materials (2021), 33, 4055.
3 Boysen N., and Devi A., Angewandte Chemie International Edition (2018), 57, 16224.
4 Devi A., and Riedl T., Advanced Materials Technologies (2022), 2200796.
5 Zanders D., et al., Advanced Materials Interfaces (2022), 2201709.
6 Wilken M., et al., Small (2022), 2204636.
7 Wree J.-L., et al., Journal of Materials Chemistry C (2021), 9, 10254.
8 Neubieser R.-M., et al., Micro and Nano Engineering (2022), 15, 100126.

ULTRASHORT PULSE LASER FOR PIONEERING 2D TECHNOLOGY

The universal tool from deposition to ablation

In the last decades lasers have established themselves as a suitable processing tool for a wide range of applications. The selective, precise, fast and contactless energy deposition into the material is an advantage over conventional machining tools and, thus, enables new processing technologies. The development of laser pulse durations in the femto – to picosecond range has opened a whole new field of application. Because of the ultrashort time duration of the laser pulses the heat expansion in the material is practically non existing. The so called "cold" energy deposition enables more precise process results and processing of new (temperature sensible) materials. Our group is investigating the possible application of these ultrashort pulse (usp) lasers in existing and emerging materials like 2D materials.

This group of materials has developed a high interest in research since the first exfoliation of graphene in 2004. Since then, the number of newly discovered 2D materials is constantly growing e.g. transition metal dichalcogenides (TMDCs), hexagonal boron nitride, black phosphorus and many more. The unique mechanical, optical, and electronical properties of the materials, which are only one to few atomic layers thick, make them promising candidates for the next generation of flexible electronics. In particular, the 2D materials graphene (as a conductor) and molybdenum disulfide (MoS_2) (as a direct or indirect semiconductor) have a high research potential and are in the focus of our research.

In our work with graphene we were able to establish an usp laser process for the reduction of graphene oxide. This enables the possibility to generate graphene-like materials in a cost-efficient and large-scale production process by irradiating dispersed graphene-oxide in a liquid film with usp laser pulses. Dependent of the laser energy and the number of pulses per site, a reduction of the graphene oxide is induced, see Figure 1 a). At higher energies, the usp laser process leads to a simultaneous nano structuring of the graphene-like material, as it can be seen in Figure 1 b). This combines a two-stage technology process by a single usp laser process [1]. Beside the production of graphene-like material usp laser enable the selective ablation of this material for macroscopic structuring. The advantage of the laser process is the possibility of free form ablation und the lack of additional coating materials like they are used during etching processes. Debris-free ablation of graphene electrodes was achieved by usp laser processing in vacuum, leading to an improvement

Prof. Dr.-Ing. habil. Andreas Ostendorf
Applied Laser Technologies
andreas.ostendorf@rub.de

Malte J. M. J. Becher
Applied Laser Technologies
malte.becher@rub.de

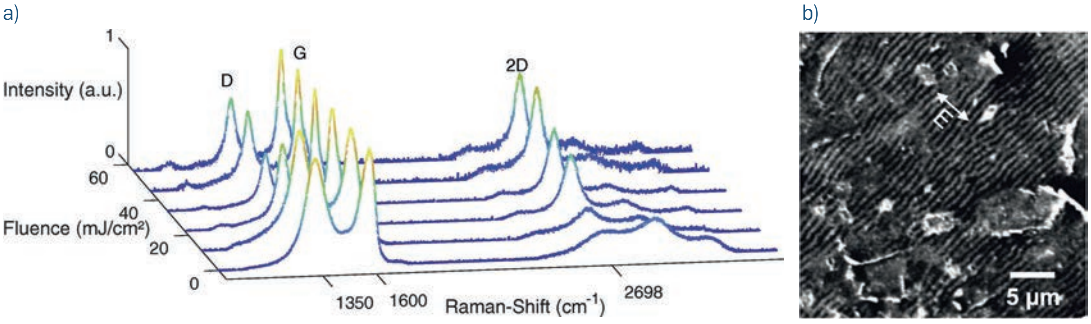


Figure 1 a): Raman spectra of unexposed GO and reduced GO with increasing femtosecond laser energy (at 10^4 number of pulses per spot) show a significant increase of 2D peak and D peak decrease, indicating reduction of GO. b) SEM image of periodic surface structures, with an average period of 800 nm, a height of 28 nm and an orientation perpendicular to the laser polarization as indicated by the white arrow on top.

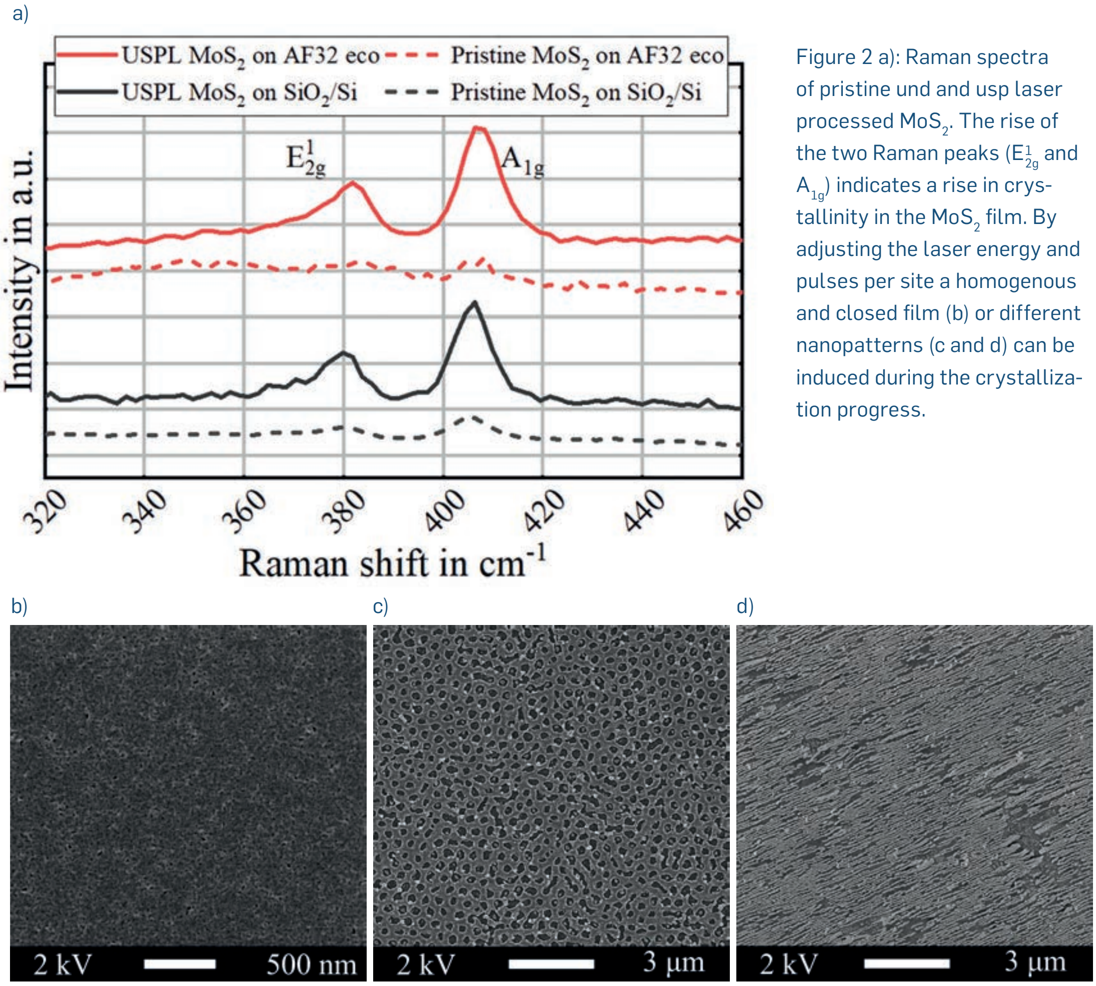


Figure 2 a): Raman spectra of pristine und and usp laser processed MoS_2. The rise of the two Raman peaks (E^1_{2g} and A_{1g}) indicates a rise in crystallinity in the MoS_2 film. By adjusting the laser energy and pulses per site a homogenous and closed film (b) or different nanopatterns (c and d) can be induced during the crystallization progress.

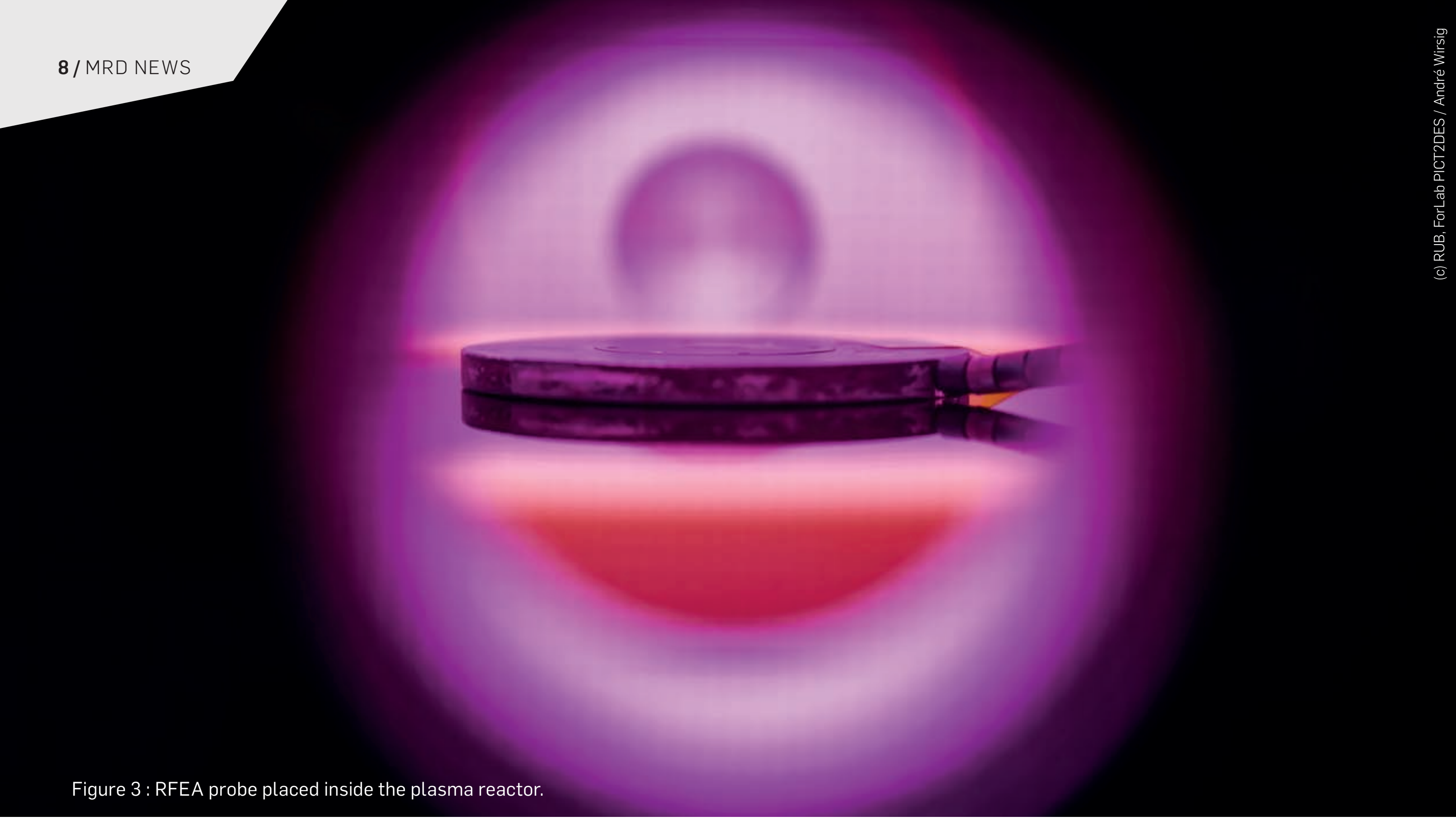
of metal-oxide thin film transistor characteristics and a reduction of the semiconductor/insulator trap density [2].

The interdisciplinary BMBF-funded project FlexTMDSense (Grant No.: 16ES1096K) as part of the ForMicro-programme comprises research on ultrathin pH and gas sensor systems based on two-dimensional (2D) semiconductor films from the TMDCs material class [3]. Our research in this project is concerned with the post treatment of the TMDC films, which are directly deposited onto flexible substrates by low-temperature atomic layer deposition (ALD). Due to the low-temperature deposition, the degree of crystallization of the TMDCs is not suitable for high-efficiency electronics. This is where the “cold” energy input of the usp laser comes into play. Through the negligible heat expansion annealing of the TMDC film becomes possible without damaging the temperature-sensitive substrate. By selecting a suitable parameter combination of laser energy and number of pulses by site we achieved an increase in the degree of crystallization in molybdenum disulfide (MoS_2) without any disruption of the film, see Figure 2 a) and b). Through an increased laser energy a simultaneous nanopatterning, similar to the graphene-oxide reduction process, is possible [4]. The formation of this nanopatterning can also be tuned to get different geometries of nanopatterning, see Figure 2 c) and d) [5]. In addition to the properties as a 2D material and the natural semiconducting phase (2H) of MoS_2 depending on the atom configuration the material possesses also a metastable metallic (1T) phase. This two-phase system enables in-plane edge contacts of the 2H and 1T phase in a single layer. Through these contacts a strong decrease of the contact resistance is possible, which increases the efficiency of the electronic devices. The usp laser provides the possibility to induce the phase transformation of the 1T into the 2H phase without the use of additional coatings, which would damage the sensible 2D material film. Additionally, the “cold” energy process by using the usp laser avoids the damage of flexible substrates [6].

To conclude, usp laser technology is a multifunctional enabler for 2D materials. The “cold” energy deposition is suitable for the generation, modification, nano- and macro-structuring of the ultrathin films. In particular, the ability to process the films directly on temperature-sensitive materials replaces time-consuming, error-prone and expensive transfer processes. Furthermore, the usp laser process eliminates the need for additional work steps and materials such as the deposition and removal of coatings that can damage the 2D material.

REFERENCES:

1 Kasischke M., et al., Applied Surface Science (2018), 445, 197-203.
2 Kasischke M., et al., Applied Surface Science (2019), 478, 299-303.
3 https://www.flextmdsense.ruhr-uni-bochum.de/
4 Becher M. J. M. J., et al., Advanced Engineering Materials (2023), 25 (21), 2300677.
5 Becher M. J. M. J., et al., Frontiers in Nanotechnology (2023), 5, 1227025.
6 Becher M. J. M. J., et al., Lasers in Manufacturing Conference (2023), 1-8.



(c) RUB, ForLab PICT2DES / André Wirsig

Figure 3 : RFEA probe placed inside the plasma reactor.

SELECTIVE ETCHING OF 2D MATERIALS

Tailoring waveforms to precisely control ion energies

Prof. Dr. Julian Schulze
Applied Electrodynamics and Plasma Technology
schulze@aept.rub.de

Florian Beckfeld
Applied Electrodynamics and Plasma Technology
beckfeld@aept.rub.de

In the design of electronics in integrated circuits, miniaturization has been the trend for decades. Reducing the feature size of a component in an integrated circuit gives room for more components in the same area, enhancing computing power. For micro-electromechanical systems, this provides the opportunity to produce components such as sensors based on less resources. With feature sizes in these components approaching a few nanometers, production processes demand for technologies that are able to control the deposition and removal of thin films on the scale of, ideally, one atomic layer. Due to this thickness, the materials addressed are referred to as "2D materials".

Low-temperature plasmas play an important role in the production of these devices. A process used for the removal of material, called plasma etching, can be imagined like this: a wafer made of a certain material (e.g. silicon), covered with a patterned mask, is placed on a substrate inside a vacuum chamber containing a gas at a pressure of about 1 Pa (Figure 1). Energy is coupled into the chamber by applying a sinusoidal voltage at radio-frequency (f = 13.56 MHz) to a coil. This ionizes the background gas, creating a plasma inside the chamber. Ions from the plasma are then accelerated towards the wafer due to a sinusoidal voltage at 13.56 MHz applied to the substrate. The ions strike the surface with high energies, etching structures into the surface where the mask is not present. To accelerate the process, reactive gases such as fluorine or chlorine can be admixed.

For a long period, this process has been continuous, meaning that the substrate got etched until a certain goal was reached and then the process was stopped. With the need for atomic layer precision, a stepwise process, so-called atomic layer etching (ALE), is implemented. In a first step a surface (e.g. silicon) is chlorinated, which leads to Si-Cl bonds which are weaker than the Si-Si bonds in the layer underneath. In a second step, these weakened Si-Cl bonds are removed through plasma etching.

When it comes to the design and control of these processes, the energy and the flux of the ions at the wafer play a key role [1-2]. When ions are accelerated onto the surface by an electric field at a frequency of 13.56 MHz, they can react to some extent to the oscillating field, leading to a

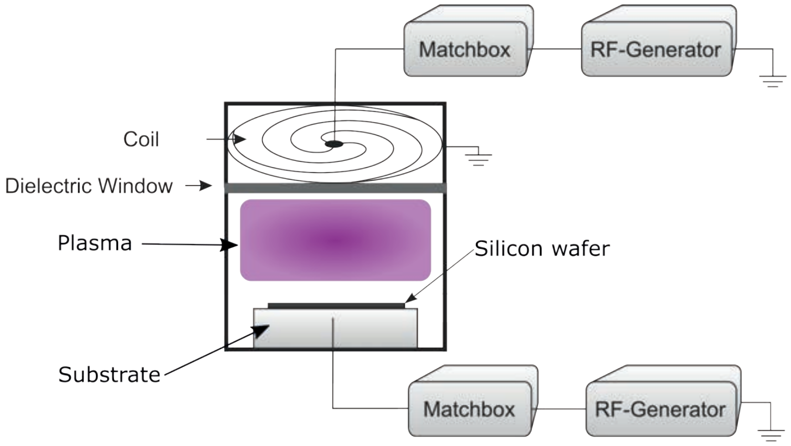


Figure 1: Sketch of a reactor commonly used for plasma etching.

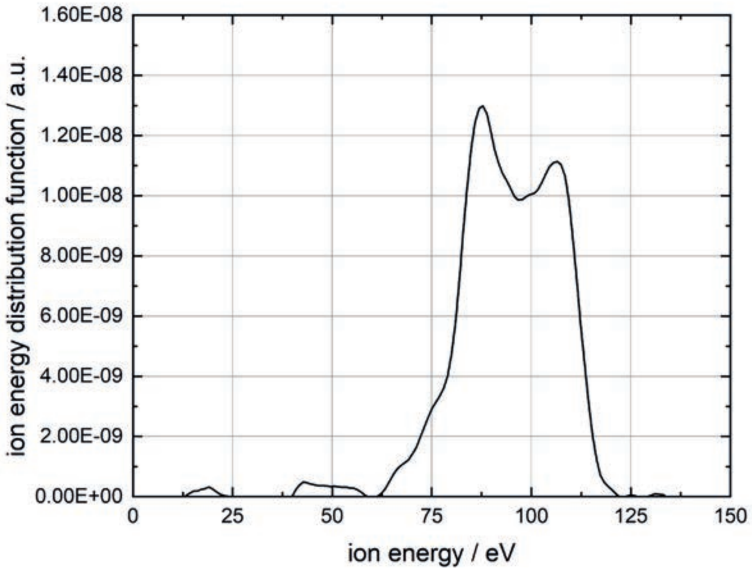


Figure 2: Ion energy distribution function measured in a plasma discharge operated at 13.56 MHz.

broad distribution (Figure 2). To be able to remove a Si-Cl layer, ions with a specific energy that break these bonds but not the Si-Si bonds underneath are needed. This range of energy is called the “ion energy window”. This ion energy window is often just a few eV broad, hence with an ion energy distribution from a classical process that uses 13.56 MHz (Figure 2) this process is less precise and inefficient.

Therefore, a technique for ion energy control with waveforms that are different from the standard of a sinusoidal waveform at 13.56 MHz, called voltage waveform tailoring, is researched by our group [3]. To achieve this, broadband power amplifiers in combination with arbitrary waveform generators are used to produce different kinds of waveforms. To analyse the results, different diagnostic tools are used to measure properties of the plasma. For example, ion energy and flux are measured by placing a probe (retarding field energy analyser, RFEA, [4],) at the surface where the wafer is usually placed (Figure 3). Other methods applied are measurements of the electron density in the plasma, which is directly linked to ion and radical densities, as it is the electrons that create these species through dissociation and ionization collisions, or mass spectroscopy to directly analyse the composition of the gas.

Through the combination of voltage waveform tailoring and diagnostic methods, a detailed understanding of the relationship between input parameters (generator power, pressure, gas composition, etc.) and plasma parameters is gained. In the frame of the research project FlexTMDSense, these insights are further correlated with etch processes to create a link between the plasma parameters and etch rates or selectivity for different materials. With this knowledge, a process can be steered in a distinct direction through plasma diagnostics, increasing the efficiency of the process.

REFERENCES:

1 Schulze J., et al., Plasma Sources Science and Technology (2011), 20, 045007.
2 Donkó Z., et al., Journal of Physics D: Applied Physics (2009), 42, 025205.
3 Rauf S., et al., Plasma Sources Science and Technology (2023), 32, 034002.
4 Ries S., et al., Review of Scientific Instruments (2021), 92, 103503.

Figure 2: ZGH clean room. The picture shows the RIE machine and parts of the grey room.

CLEAN ROOM

The sanctuary of the micro-realm

Dr. Dennis Naujoks
Center for Interface-Dominated High-Performance Materials
dennis.naujoks@rub.de

Dr. Philip Schmitt
Microsystems Technology
philip.schmitt@rub.de

In the world of material science, highly controlled environments are crucial for conducting experiments and fabricating materials with exceptional precision at the atomic and molecular levels. Hence, clean rooms, where precision and purity reign supreme, serve as indispensable sanctuaries of the micro-realm. From semiconductor fabrication to nanotechnology development, clean rooms form the backbone of countless industries, facilitating the production of cutting-edge materials and technologies that shape our modern world.

The clean room in the ZGH (Center for Interface-Dominated High-Performance Materials) extends over an area of 300 m² and contains a variety of laboratories for processing and analysis of micro and nano systems. It was constructed according to the ISO 14644 standard. As a part of this the cleanliness is meticulously regulated for every laboratory, reaching up to the ISO 5 level in the lithography. To better comprehend the extent of cleanliness within the clean room, envision a cubic meter of air within a typical laboratory setting. This volume of air typically contains 100.000.000 particles measuring 0.3 µm (similar in size to a corona virus) and 300.000 particles sized 5 µm (comparable to pollen). However, within an ISO 5 clean room, the permissible particle count per cubic meter drastically diminishes to just 102,000 for particles sized 0.3 µm and zero for particles 5 µm and larger. To put these particle sizes in relation: A human hair is still 10 to 30 times thicker than the 5 µm pollen. Achieving such a degree of purity requires a sophisticated airflow management system. The cleanroom ventilation systems utilize high-efficiency particulate air (HEPA) filters to remove airborne particles. These filters are strategically positioned in the ceiling of the clean room laboratories to create laminar airflow patterns that direct particles away from critical areas. Additionally, airflow velocity, direction, and pressure differentials are carefully regulated to prevent the ingress of contaminants and maintain the desired cleanliness class.

The focal point of ZGH's cleanroom is its lithography facility. Upon entering the lithography laboratory, one immediately notices the yellow lighting, essential for protecting the UV-sensitive photoresist utilized in the photolithographic process, which enables the precise transfer of patterns onto substrates. This intricate procedure entails multiple steps and relies on specialized equipment such as spin coaters, heating plates, a UV mask aligner, and development baths. The resulting resist mask can be used in subsequent processes to deposit or etch specific structures onto the substrate. The ZGH cleanroom provides

Figure 1: Micro sized RUB word cloud made from silicon via DRIE.

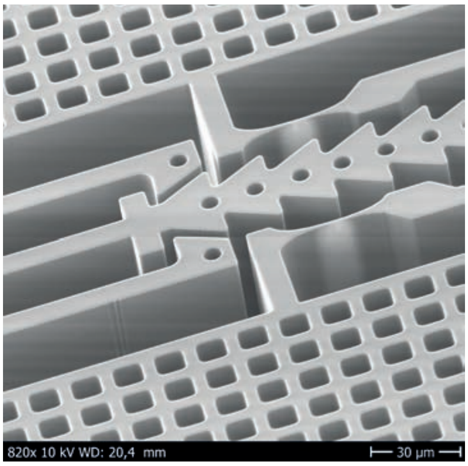


Figure 3: Micromechanical memory of a passive acceleration sensor. Fabricated by DRIE in Silicon (Design by P. Schmitt).

a range of techniques for this purpose. Thin films can be deposited using either PECVD (plasma-enhanced chemical vapor deposition) or PVD (physical vapor deposition). In addition to conventional wet etching methods involving KOH or HF, substrates can be structured through dry etching in one of ZGH's three plasma etch reactors. These plasma machines from Oxford Instruments offer capabilities such as RIE (reactive ion etching), RIBE (reactive ion beam etching), or DRIE (deep reactive ion etching).

The ZGH functions as a research center providing office and lab space for up to 80 researchers engaged in collaborative research endeavors under the ZGH research program. Utilizing the facilities and machinery available, researchers at ZGH can conduct experiments or fabricate microsystems. For instance, Dr. Philip Schmitt from the Chair of Microsystems Technology used the DRIE machine during his doctoral studies to fabricate a micromechanical acceleration sensor. By incorporating elements like a mechanical amplifier, mechanical memory, and a mechanical analog-to-digital converter—typically discrete components—into a single package superior efficiency for this sensor was achieved. A section of the mechanical memory, resembling a microscale ratchet jack, is depicted in the SEM image (Figure 3). The high aspect ratios necessary for this micromechanical system can be achieved by cyclically alternating between etching and passivation phases (see Figure 4). During the etching phase, a high-energy radio frequency plasma transforms SF_6 as etching gas into a reactive plasma. The etching mechanism itself is a combination of chemical and physical etching reaction by accelerated Flour radicals of the SF6 plasma. In combination, the etching process is slightly anisotropic. Once a defined depth is reached, the process transitions to the passivation phase. Here, a thin polymer-like passivation layer is deposited on the surface and the sidewalls of the etched features by activating C_4F_8 with the plasma source. This passivation layer acts as a protective barrier, preventing further lateral etching and allowing for deeper etching to occur in subsequent cycles. Due to the slight anisotropy of the etching step combined with the repeated deposition of the protective layer each iteration of the loop incrementally deepens the features while maintaining sidewall integrity and preventing the etching from spreading laterally.

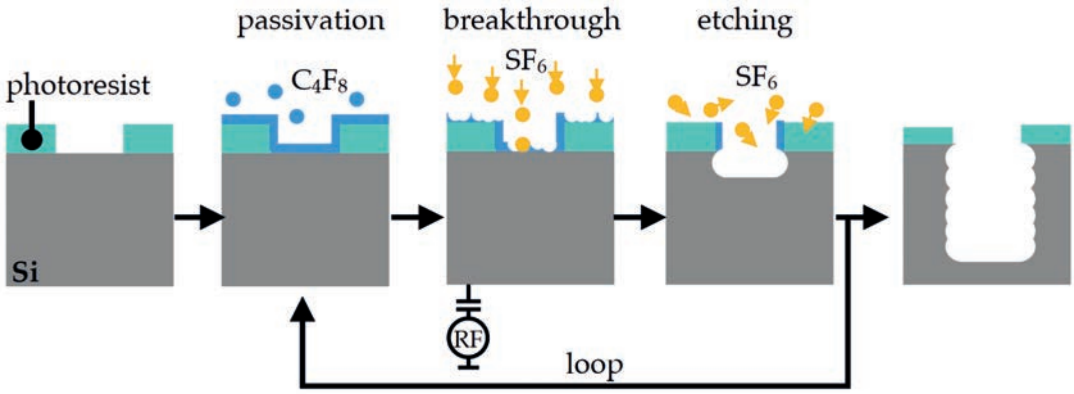


Figure 4: Schematic representation of the DRIE process.

REFERENCES:

1 Schmitt P., and Hoffmann M., Microsystems & Nanoengineering (2023), 9, 83.

2 Schmitt P., and Hoffmann M., IEEE International Conference on Omni-layer Intelligent Systems (COINS), Berlin, Germany, (2023), 1-5.

(c) RUB, ForLab PICT2DES / André Wirsig

Figure 1: Customer-specific five chamber Cluster-tool installed within the cleanroom of the ForLab Bochum.

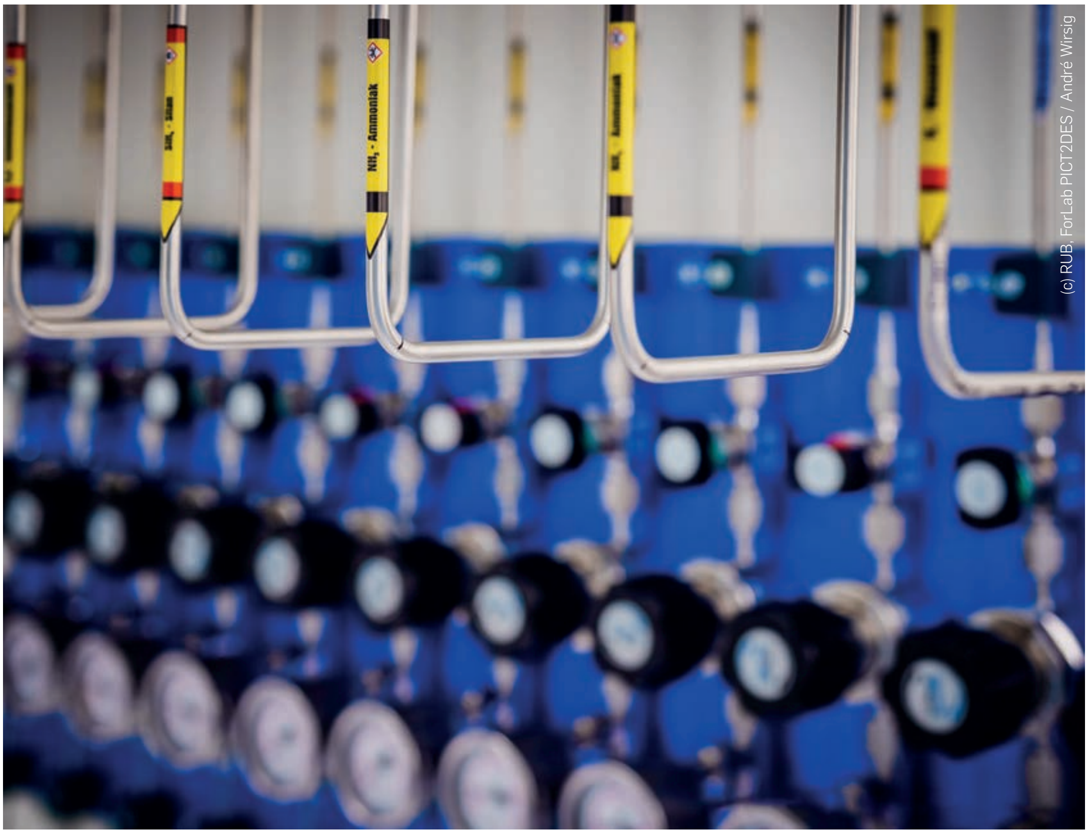
THE FORLAB BOCHUM

From idea to application and beyond

Prof. Dr. Martin Hoffmann
Microsystems Technology
martin.hoffmann-mst@rub.de

The invention of new materials becomes an innovation that influences our daily life with the introduction into systems and applications. But also requires the transfer from a demonstration on a single device to a scalable technology as well as the demonstration of the robustness that is required for a reliable application. A key step is the transfer of new materials or processes on a wafer scale process. Carbon nanotubes have been fabricated in the 70th [1] and it was shown in the 90th of the last century that carbon nanotubes (CNT) exhibit extraordinary performance [2], but until today a technology to fabricate billions of well-aligned CNT transistors on a wafer is missing. In the meantime, graphene had been demonstrated and subsequently, new 2D materials but even more fancy properties have been introduced. Actually, the properties of Graphen have been described before the CNT in 1947 [3], but were never validated until the 21st century [4]. But how to produce full wafer scale films replacing micrometer-sized single flakes?

A team of scientists (Claudia Bock, Anjana Devi, Peter Awakowicz, Julian Schulze and Martin Hoffmann) applied for a five-chamber ALD / ALE system within the ForLab program of the BMBF for state-of-the-art infrastructure. The system was granted (ForLab PICT2DES – a Process Integrating Cluster Tool for 2D Electronic Systems, Grant No.: 16ES0941) and established between 2019 and 2022 (Figure 1). The configuration of the cluster tool is complex, and the cluster tool required 14 process gas lines, 42 process gas inlets, and around 300 metres of stainless-steel pipework for the gas supply (Figure 2). In addition, an exhaust gas purification system (a dry bed absorber as a triple column system) and a gas monitoring system had to be fully integrated into the safety infrastructure of the cleanroom, as Cl-based gases, H2S and silane as well as highly flammable and toxic ALD precursors are potentially hazardous. First applications of the operational cluster tool are presented in other contributions of this newsletter.



(c) RUB, ForLab PICT2DES / André Wirsig

Figure 2: The cluster tool requires an elaborate, complex infrastructure, particularly in the area of gas supply and exhaust gas treatment.

The unique selling point is the integration of different processes required for 2D system integration into a single machine that allows a wafer scale processing (deposition and etching) without disruption of vacuum. Thin 2D films are highly sensitive to environmental conditions. Moreover, the system handles substrates up to 200 mm diameter – silicon wafers, glass plates and foils down to 30 µm and polymer sheets. Consequently, this demands for a fabrication line for 200 mm substrates at all process stages, e.g. wet processing, metallization and lithography. Such a facility requires concepts for a broad use from basic research to applications including commercial cooperations that mirror expectations into basic research, including reliability, scalability and technical as well as environmental issues. Unfortunately, the discovery of a new effect is good for 80 % of the merits, but it includes approx. 20 % of the works required for a validation of a successful use in applications. In parallel, the cleanroom facility at Microsystems Technology also offers common MEMS processes on 100 and 200 mm Si substrates in cooperation with ZGH (Center for Interface-Dominated High Performance Materials).

Meanwhile, the BMBF ForLab program developed into a Germany-wide network of cleanroom facilities at Universities [5]. It aims for intensified cooperations between the research partners, but also addresses the transfer into applications bridging the “death valley” between fundamental research inventions and innovative applications. In 2023, the follow-up project ForLab NataliE (Grant No.: 16ME0873) was started by the BMBF that is conducted by TU Dresden, TU Ilmenau and RUB. This project addresses non-scientific aspects such as cooperation, financial concepts and young talent recruitment. The boom in semiconductor manufacturing in Europe and in Germany needs highly skilled stuff, but the count of engineering students is continuously decreasing. Therefore, initiatives have to demonstrate that buzzwords such as digitalization, energy transition or autonomous driving not only require informatics, but also advanced electrical hardware based on state-of-the-art materials and technologies.

Bringing together about 20 Universities that are active in the field of microelectronics and microsystems showed that all face similar challenges as described before. The ForLab consortium is establishing an organizational structure for research at universities comparable to the FMD (Forschungsfabrik Mikroelektronik Deutschland) for the non-academic research institutes.

One highlight is the Mikrosystemtechnik-Kongress 2025 organized by BMBF and VDE in Duisburg and jointly chaired by Anton Grabmaier (FhG IMS) and Martin Hoffmann (RUB).

Hopefully, many results of RUB research will be on display at this largest national event for microelectronics and microsystems technology, where also the big industrial players are present.

REFERENCES:

1 Oberlin A., et al., Journal of Crystal Growth (1976), 32 (3), 335–349.
2 Wilder J. W., et al., Nature (1998), 391 (6662), 59–62.
3 Wallace P. R., Physical Review (1947), 71 (9), 622–63.
4 Geim A., and Novoselov K., Nature Materials (2007), 6, 183–191.
5 https://www.forlab.tech/

ADVANCED PROCESS INTEGRATION **OF 2D MATERIALS**

Boosting the performance of next-generation devices

2D Materials can exhibit some incredible properties, but most of them have been only explored on a laboratory scale so far. Whether and when 2D materials will find their way into high-tech industry mainly depends on their successful large-area integration on wafer scale. 2D materials offer the possibility of van der Waals epitaxy, eliminating the restrictive material selection due to lattice mismatch which is found in conventional semiconductor epitaxy. This means that the films can also be grown on innovative, e.g. flexible substrates and therefore unlock completely new market segments such as flexible and transparent electronics, which is inaccessible to rigid silicon. This research area is the subject of the transdisciplinary FlexTMDSense project [1], which is funded by the BMBF (Grant No.: 16ES1096K). The project aims to master the advanced process development for the integration of 2D materials at wafer level for flexible sensors. This requires disruptive processes that match the low temperature budget of the flexible substrates. Bridging the valley of death from flake to 200 mm production of reliable devices requires central building blocks schematically depicted in Figure 1 and an interdisciplinary research team. The process sequences developed in this way enable a direct connection to the “Forschungsfabrik Mikroelektronik Deutschland” and thus a fast production of small series.

A homogeneous monolayer-precise deposition technology which does not affect the underlying layer is the basis for a new disruptive 2D technology. For this, the realization at low temperatures is of crucial importance. High-precision process control is essential for 2D materials, as the band gap of many 2D materials and the transition from a direct to an indirect band structure depends on the number of layers. In the PEALD chamber of the ForLab Bochum cluster tool we were able to develop a PEALD process for MoS_2 on 200 mm glass and 200 mm SiO2/Si wafers at substrate temperatures of only 230 °C [2], which leads to homogeneous coverage and direct polycrystalline growth on the entire wafer. The film-quality is sensitive to deposition chemistry as well as the type and pretreatment of the substrate [4]. This is illustrated by the layer thickness distribution of a PEALD-deposited MoS_2 layer on an ozone-treated and a plasma-treated wafer (Figure 2). To protect the sensitive ultra-thin 2D films from degradation, the films were passivated directly after deposition, without loss of vacuum. An ALD process for the deposition of a high permit-

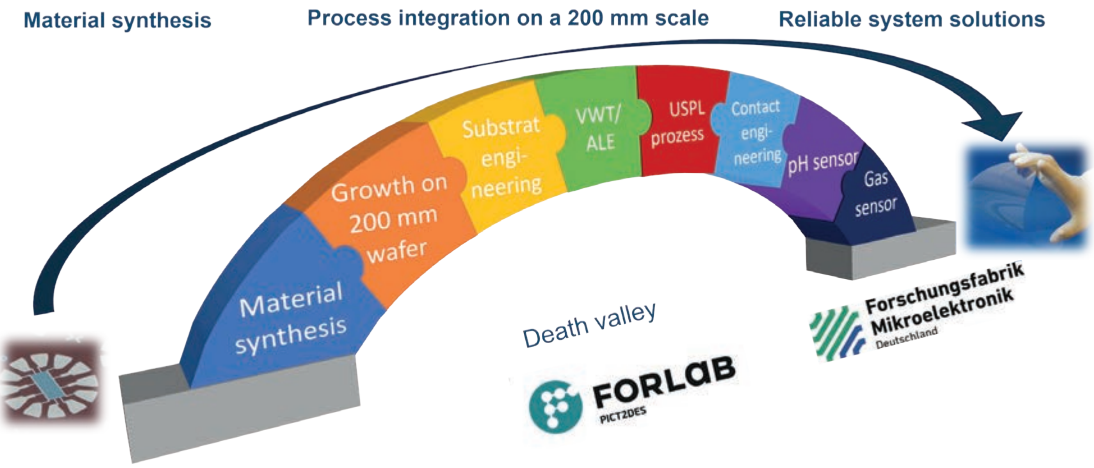


Figure 1: Central building blocks for bridging the valley of death as developed within the FlexTMDSense project for the application field of flexible sensor technology.

Dr.-Ing. Claudia Bock
Microsystems Technology
claudia.bock@rub.de

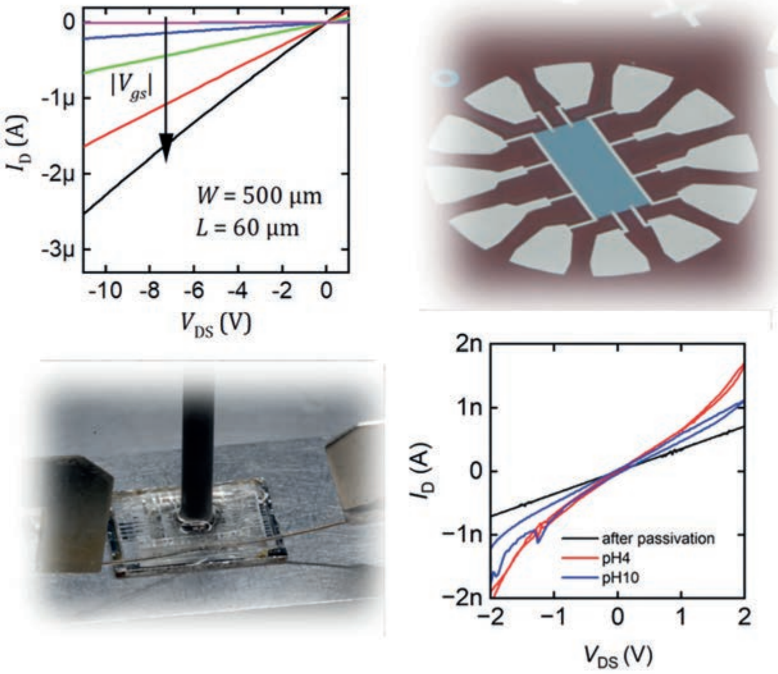


Figure 2: Ellipsometric mapping of a 200 mm wafer deposited with MoS2. The wafers were ozone (left) and plasma (right) pre-treated.

tivity gate dielectric [4] combines the aspects of passivation and functionality.

In addition to an accurate deposition, successful device preparation also requires a monolayer-precise, low-damage removal of the thin passivation layer for contacting the 2D film. Atomic-layer etching (ALE) is a suitable technique to meet these requirements. ALE comprises a fast-switching alternating sequence of self-limiting chemical modification steps affecting only the top atomic layers of the wafer, and plasma etching steps, which remove only the chemically modified areas. Together with our industrial partner Sentech Industries GmbH we developed an ALE process for Al2O3 with a sub-nm etch rate per cycle in the cluster tool [5].

Another key issue to improve the performance of devices based on 2D materials is the reduction of contact resistance. Compared to monocrystalline films low impedance contacts on polycrystalline films are even more demanding. MoS$_2$ forms both a semiconducting 2H-phase and a metastable metallic 1T-phase, which allows a new type of in-plane phase change contact. As already demonstrated for exfoliated MoS$_2$ flakes, but not yet for ALD deposited MoS$_2$ films, phase engineering can markedly reduce the contact resistance between the source/drain electrodes and the channel enabling high performance transistors. In a close collaboration with the chair of Applied Laser Technologies phase contacts will be implemented in large area ALD films.

Generally, advanced process development requires comprehensive characterization of the ALD layer before and after each process step. To this end, we use the multiple possibilities of our ForLab Bochum (Grant No.: 16ES0941) cleanroom including the process integrating five-chamber cluster tool (title page) and closely work with our project partners in the FlexTMDSense project and the central facilities of the RUB (ZGH and RUBION, see MRD Newsletter No. 16).

In a last step we combine and optimize individual processes to obtain complete process sequences, considering surface reactions, temperature budgets, cross-contamination, doping, etc. in close regard to the requirements of the application. Figure 4 depicts a transistor structure and a pH-sensor based on 2D-PEALD MoS$_2$ films with the typical IV characteristics. The process sequences are both optimized with respect to performance, longtime stability, and reproducibility.

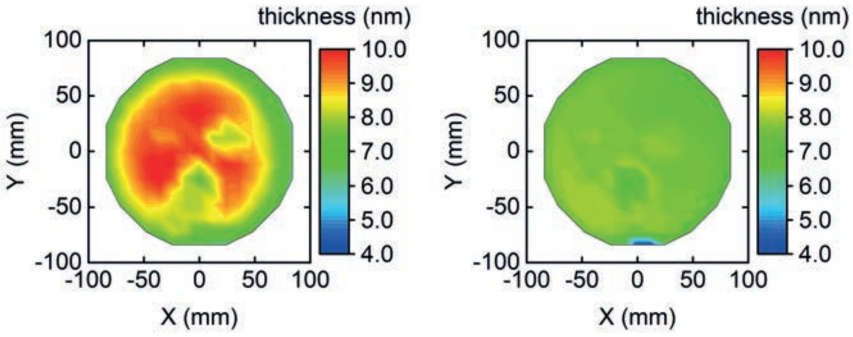


Figure 3: Examples of prepared transistor structures and pH sensors with integrated 2D film and typical IV-characteristics.

REFERENCES:

1 https://www.flextmdsense.ruhr-uni-bochum.de/index.html; https://www.elektronikforschung.de/projekte/formikro-flextmdsense
2 Jagosz J., et al., GMM-Fachbericht 105: Mikro-Nano-Integration (2022), VDE-Verlag, 8-11.
3 Berning T., et al., Materials Research Express (2022), 9, 116401.
4 Preischel F., Advanced Materials Interfaces (2023), 10 (28), 2300244.
5 https://siliconsemiconductor.net/article/118732/Wafer-level_Integration_Changes_of_ALD_for_2D_Materials?sentech

MICROMECHANICAL TENSILE TESTING **ON CHIP-LEVEL**

Investigating the mechanical properties of MEMS-Materials

Dr. Philip Schmitt
Microsystems Technology
philip.schmitt@rub.de

Prof. Dr. Martin Hoffmann
Microsystems Technology
martin.hoffmann-mst@rub.de

Tensile testing has become a standardized procedure for determining the Young's modulus and yield strength of materials such as steel, aluminum, or polymers. However, conventional tensile testing is typically conducted on macroscopic specimens in the millimeter range. But what about materials on a much smaller scale? In microsystems technology, we develop micromachines that are significantly smaller than the grain size of steel.

Due to factors such as deposition methods of thin films, resulting grain size, stoichiometry, and surface properties, the material parameters for MEMS (Microelectromechanical Systems) materials cannot simply be extrapolated from macroscopic test results.

Moreover, in microsystems technology, we come across novel materials that do not have counterparts in the macroscopic world, such as 2D materials or specialized polymers, such as photoresist, that lack practical relevance outside the micro world.

To determine the mechanical properties of thin layers, often specimens of the thin film materials are initially deposited onto a substrate, released, and then characterized on a miniaturized tensile testing machine [1]. Handling and clamping such small and delicate material specimens can be often challenging and may lead to damage to the specimen, potentially resulting in distorted measurement results. Therefore, we developed a micromechanical mechanism to perform classical tensile testing on a silicon chip. The material to be tested is directly deposited and patterned on the chip itself using the typical deposition methods of microfabrication, such as Lithography, PVD or PECVD. The stress-strain diagram of the deposited material can be determined visually with a microscope. Figure 1 shows the setup of the test mechanism.

The microsystem [2, 3] consists of the material sample to be measured and a silicon mechanism composed of a linear spring, two lever amplifiers and an input element. The tensile specimen is clamped at one end to the chip frame, while the free end is connected to the linear spring of the mechanism. The required testing force is provided externally by imposing a displacement at the input element by a needle. The force-generator converts this displacement into a force which is then applied at the free end of the specimen. By increasing the external displacement, the specimen is continuously extended. Since the resulting extension and thus the strain is quite small and difficult to detect visually, a lever-amplifier (green) is used to increase the slight strain signal of the specimen into a large output displacement. Consequently, the measured and amplified strain signal can be evaluated visually at the strain indicator.

For measuring the externally imposed force and thus the resulting stress at the specimen, a second mechanical amplifier (black) is used. The mechanism works as a differential amplifier which converts the expansion of the linear spring into a large output displacement at the force-indicator. By visual evaluation of the strain and force-indicator, the imposed force (mech. stress) and the resulting elongation (strain) can be read out simultaneously,

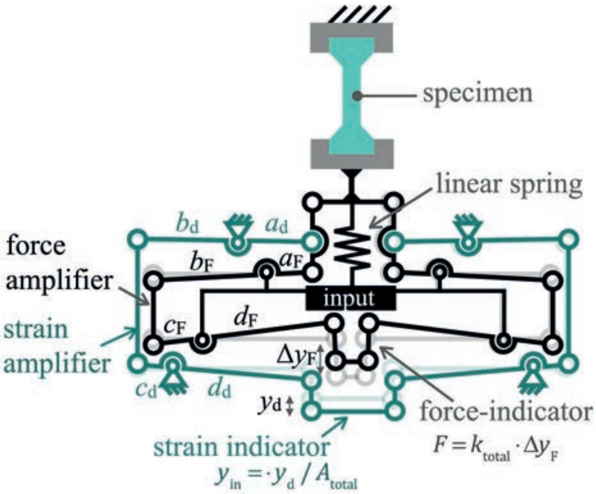


Figure 1: Schematic showing the working principle of the test mechanism.

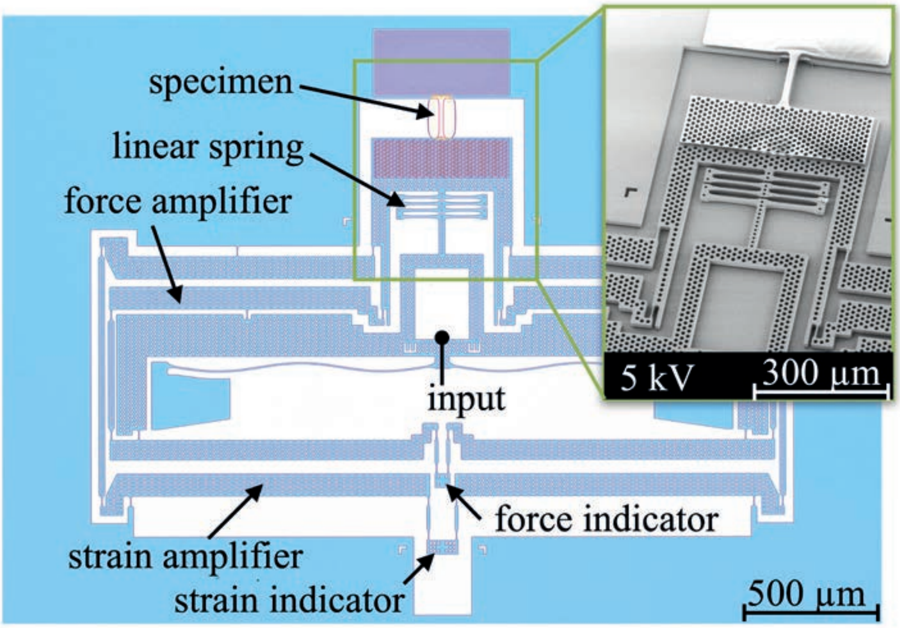


Figure 2: Microscope and SEM image of a fabricated chip for in-situ tensile testing of a polymer.

while applying an external force/ displacement at the specimen.

A specimen of photoresist (AZ 10 XT) was examined as an exemplary material sample. Since photoresist is usually not used as a mechanical material, its mechanical properties are not known. Figure 2 shows a microscope and SEM image of the fabricated test chip for tensile testing. The fabrication is performed on wafer-level, resulting in the fabrication of about 200 chips within one process run. The critical part of the fabrication is the deposition of the test material. The specimen has to be clamped on both sides and the silicon under the specimen has to be removed. By using a special isotropic etching process, we were able to release the specimen and to selectively etch the silicon without damaging the sample above. The fabrication involves typical semi-conductor fabrication processes such as DRIE, RIE, PVD and lithography. The clean room facilities of both ForLab Bochum and ZGH are used for the fabrication.

For the characterization of the test material, the chips are mounted on a Peltier element to perform the tensile tests at a controlled and constant temperature. The measurement can be evaluated visually with a microscope as shown in Figure 3a: To impose the required tensile force, the system's input on the chip is deflected by a needle mounted to an external piezo actuator. The specimen then undergoes deformation, and the resulting displacements at the force and displacement indicators of the microsystem are captured by a microscope camera. Employing tracking software, the displacements at the outputs of the lever amplifiers are visually evaluated. This analysis finally allows the determination of stress-strain characteristics and material properties, including Young's modulus, as illustrated in Figure 3b.

This research was funded by the BMBF under grant no. 16ES1063.

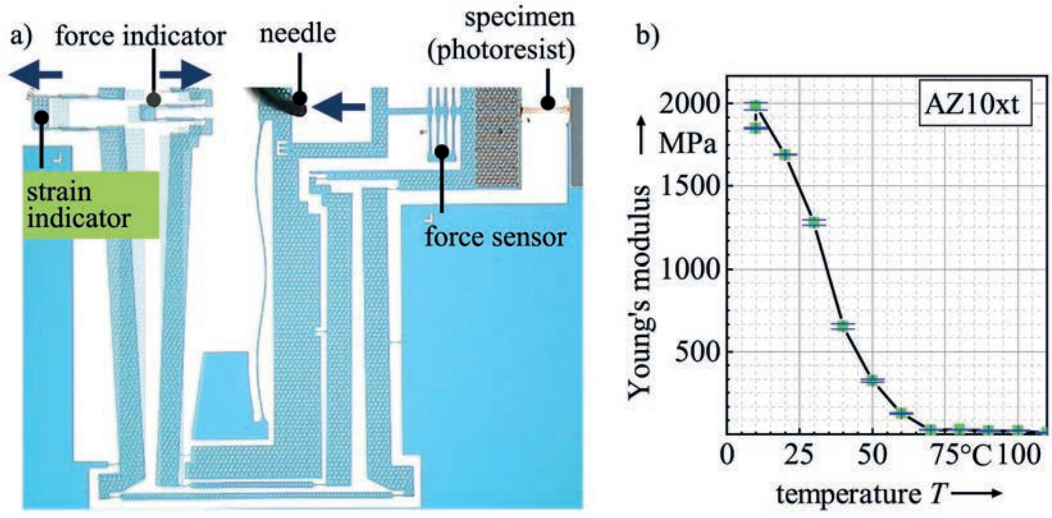


Figure 3: a) Microscope image of an actuated test device. b) corresponding measurement results for the Young's modulus of the tested polymer as a function of temperature

REFERENCES:

1 Oellers T., et al., ACS combinatorial science (2020), 22 (3), 142-149.
2 Schmitt P., and Hoffmann M., IEEE 35th International Conference on Micro Electro Mechanical Systems Conference (MEMS). (2022), 691-694.
3 Schmitt P., et al., MikroSystemTechnik Kongress (2023), 23 -25.10, Dresden.

ICME OF ELECTRICAL CONTACTS FOR THERMOELECTRIC DEVICES

Integrated Computational Materials Engineering (ICME) for high energy efficiency

Thermoelectric (TE) materials are capable of generating electricity from temperature differences by transforming part of the passing heat flux into electrical power through the solid-state Seebeck effect [1]. A strong Seebeck effect represents an as high as possible voltage generated by a temperature difference between hot and cold side of a thermoelectric material sample. The TE material's performance is characterized by the TE figure of merit, *zT*, that depends on the absolute temperature (*T*) and on the temperature dependent electrical (σ) and thermal conductivity (*K*) and the Seebeck coefficient (S) as displayed in Eq 1.

$$zT=\frac{(\sigma\ S^2)}{K}T$$

Desirably high Seebeck coefficient values can be achieved by semiconductor materials that have a suitable electronic band structure featuring multiple band extrema of low curvature (equivalent to a high charge carrier effective mass) located adjacent to a small band gap, as shown in Figure 1. The Seebeck coefficient depends on temperature, composition of the semiconductor materials, and the electronic chemical potential so that performant TE materials are sensitive to the band gap energy and the masses of electrons and holes [1].

A thermoelectric generator (TEG) is an energy harvester and supplier by direct conversion of thermal into electrical energy. In service, no harmful emission occurs which makes TE technology attractive for green energy applications. Another important advantage is the absence of mechanically moving parts which allows for operating a TEG free of maintenance. Therefore, TEGs find multiple applications as power supply for autonomous systems in critical locations, where maintenance is difficult or impossible. Examples are power suppliers for space applications or for extreme conditions on Earth to recover waste heat in industries such as steel plants. Vice versa, with voltage supply, TE devices are able to carry heat with the passing electrical current, thus acting as a heat pump, cooling one side but heating the other [3].

Despite their promising sustainable applications, there is no established mass production of high temperature TEGs yet. Reasons are the challenging design and optimization of the TE material itself as well as development of tailored TE devices for each application. Further, long-term stable TE materials from non-toxic, abundant, and inexpensive elements are needed as well as long-term stable contacts for ensuring mechanical integrity and functionality of the device. A standard TEG architecture consists of several pairs of thermoelectric material "legs" of n- and p-type semiconductors working under a thermal gradient between a hot, heat-absorbing side and the cold sink side, as shown in Figure 1. To minimize electrical and thermal losses, material specific TE material/metal junctions need to be developed, enabling unhindered heat and current flow through the legs. Individual legs are connected electrically in series through metallic bridges and all legs are stacked between electrically insulating layers such as ceramic plates.

Poor TE material/metal junctions can easily lead to significant performance losses and complete failure. We are therefore focusing on mastering the challenges of this interconnection zone (IZ) between the TE material/electrode. The IZ is a region that may develop multiple intermetallic layers with complex morphologies, as well as new moving interfaces. As an entity, the IZ has to satisfy mechanical constraints without hindering the conversion performance and functional stability of the TE material.

However, the contacts affect the functionality of the TE material by diffusion and reaction mechanisms responsible for phase transformations at the interfaces and growth of intermetallic layers in the IZ. Strong diffusion of electrode or TE material atoms across the IZ may have a severe detrimental effect on the Seebeck coefficient of the TE material as a result of an unintended (counter) doping effect that shifts the carrier concentration of the

Dr. Silvana Tumminello
German Aerospace Center
silvana.tumminello@dlr.de

Dr. h.c. Dr. Suzana G. Fries
Materials Research Department, RUB
suzana.g.fries@rub.de

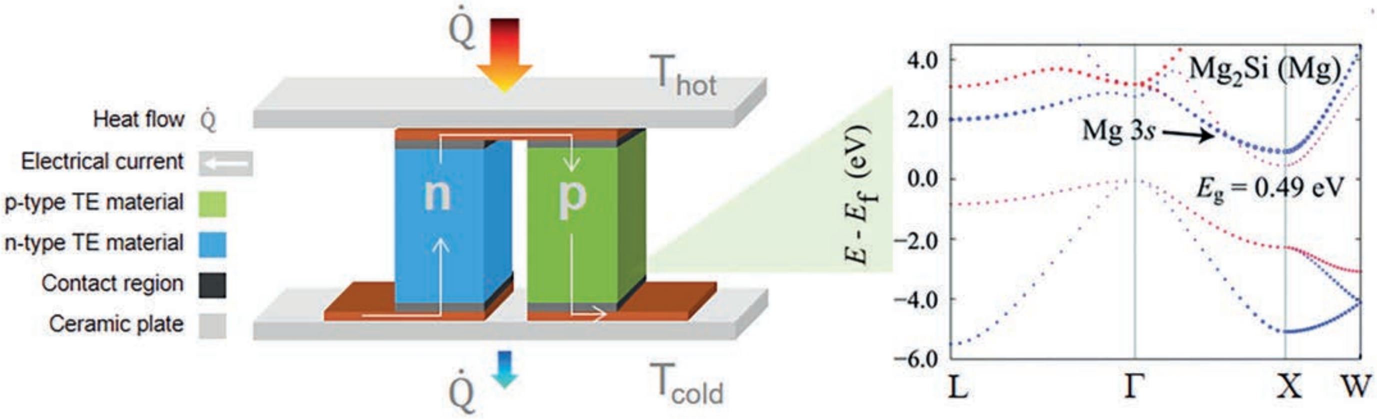


Figure 1: Thermoelectric module and calculated electronic band structure of the semiconductor Mg_2Si thermoelectric material with Eg indirect band gap energy, adapted from [2].

converter material from its optimized value [4]. To avoid uncontrolled diffusion, a typical solution is sputtering of diffusion barriers specifically suitable for the individual TE/electrode combination. However, this often reduces the bonding strength, increases contact resistances and chemical complexity at the IZ.

Phase diagrams are valuable to understand chemical and microstructural changes happening in the contact region under long-term operation conditions (high temperature and thermal cycles) and even more, allow to anticipate chemistry and microstructure evolution at interfaces during the contacting process. As in the example shown in Figure 2, in $Mg_2(Si_{0.3}Sn_{0.7})$/Cu contacts, the strong diffusion of Cu into the $Mg_2(Si_{0.3}Sn_{0.7})$ material is evidenced by the changed Seebeck coefficient measured after contacting (indicating a decrease of the previously optimized carrier concentration and figure of merit) and resulting in the formation of a quaternary Laves phase, C15, in the IZ in agreement with the calculated phase diagram [5].

The mechanical aspect in the development of TE materials and contacts has earned much less attention than the TE properties. However, mechanical properties of the TE materials and the contacts must be considered to make useful devices. At the IZ, low thermal and electrical resistances are important but also matching thermal expansion of TE, bonding layers, and electrode as well as high bonding strength under thermal gradients and cycles.

The compatibility of chemical, mechanical and thermal properties of all TE components is crucial

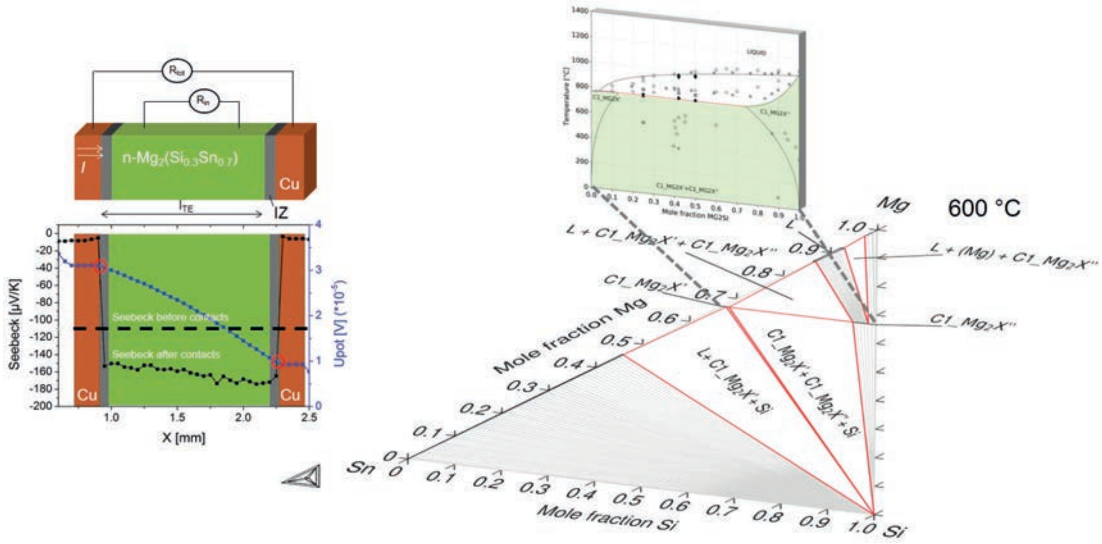


Figure 2. Left: Spatially resolved measurement of the Seebeck coefficient and the electrical potential across a contacted TE leg: the Seebeck coefficient measurement indicates the exact interface position and a material change compared to before contacting while the potential drops across the interfaces indicates the electrical contact resistance.
Right: Calculated ternary phase diagram for Mg-Si-Sn at 600 °C and Mg^2Sn-Mg_2Si isopleth with a thermodynamic database compiled with data from [6]. Green shadow indicates where the TE material is stable in the phase diagrams.

Prof. Dr.-Ing. Marion Bartsch
German Aerospace Center & Materials Research Department, RUB
marion.bartsch@dlr.de

Prof. Dr. Eckhard Müller
German Aerospace Center & Justus Liebig University Giessen
eckhard.mueller@dlr.de

Jun.-Prof. Dr. Johannes de Boor
German Aerospace Center & University of Duisburg-Essen NST@UDE
johannes.deboor@dlr.de

to avoid crack formation. Cracks naturally interrupt the electrical and thermal circuit and further crack propagation leads to the assembly failure and fracture of the TE leg.

Mechanical properties are impaired by changes in the microstructure and phase composition of the IZ and adjacent TE material, which occur during service because of chemical instability. Therefore, an integrated approach is needed including thermodynamic, kinetic and mechanical design. Figure 3 shows on the left an exemplary microstructure of the IZ between Cu contact and the n-type TE material n-$Mg_2(Si_{0.3}Sn_{0.7})$ which developed due to strong Cu diffusion. On the right a SEM image of a TE leg shows failure by fracture of the semiconductor leg adjacent to the contact to the metallic bridge.

For finding an optimized geometry of a basic TEG module which allows for integrated optimization with numerical tools, considering thermoelectric efficiency as well as structural integrity, parametrized models have to be developed. After preselection of an optimized geometry, prototypes are assembled and tested. Finally, modules are coupled with heat source and heat sink inside bigger devices such as a Moon rover, or on the Earth in cars or industrial plants. Figure 4 illustrates the development steps from TE to application.

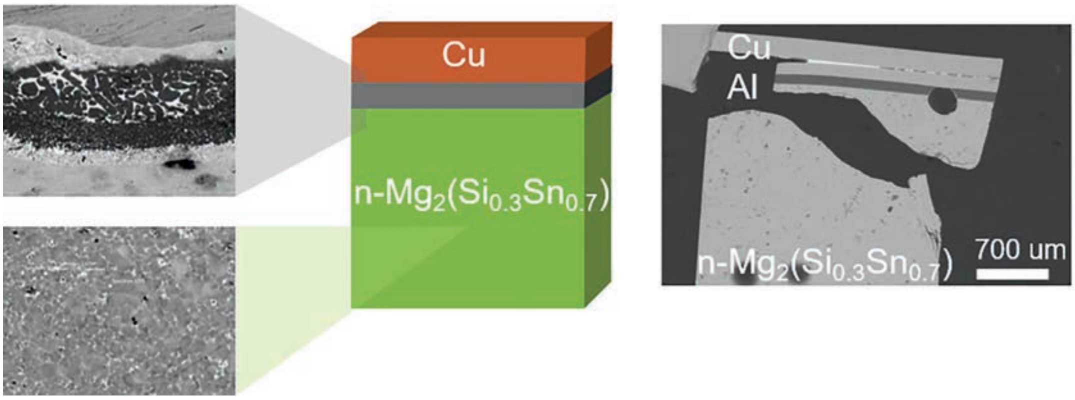


Figure 3. Left: micrograph of the IZ between contact and n-type TE material (top) and the unaffected TE material (bottom), adapted from [4]. Right: SEM image of a TE leg fracture near the contact to the metallic bridge, $Mg_2(Si_{0.3}Sn_{0.7})$ is the TE material with Al as inner contacting layer and Cu as outer layer and bridge.

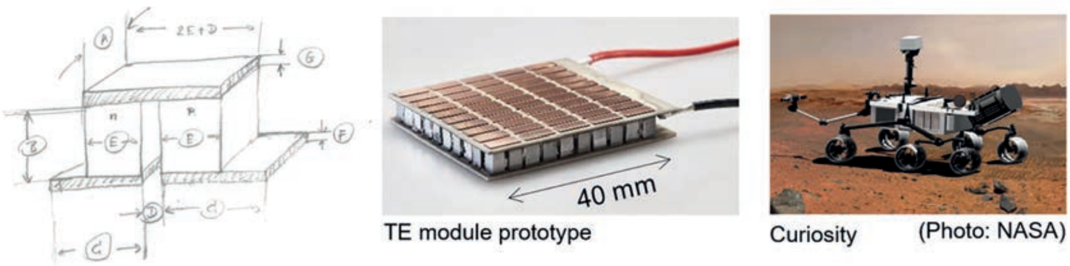


Figure 4: Principal steps from initial design with parametrization of a basic TE to a prototype TEG and integration of TEG devices in a Mars rover.

REFERENCES:

1 Snyder G., and Toberer E., Nature Materials (2008), 7, 105-114.
2 Kim C.-E., et al., Physical Chemistry Chemical Physics (2016), 18, 2, 939–946.
3 Zhu T., et al., Advanced Materials (2017), 29, 14, 1605884.
4 Ayachi S., et al., Advanced Physics Research (2024), 3, 2300077.
5 Tumminello S., et al., Journal of Materials Chemistry A (2021), 9, 36, 20436–20452.
6 Kozlov A., et al., Journal of Alloys and Compounds (2011), 509, 7, 3326–3337.

Materials
Research
Department

CONTACT

Materials Research Department
Universitätsstr. 150
D-44801 Bochum

@ mrd@rub.de
↗ www.mrd.rub.de