Defects in Two-dimensional Materials

750. WE-Heraeus-Seminar

08 May - 12 May 2023

at the Physikzentrum Bad Honnef, Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Subject to alterations!

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 750. WE-Heraeus-Seminar:

Defects in crystalline solids are ubiquitous. It is the second law of thermodynamics that gives rise to the appearance of a certain amount of disorder in materials at finite temperatures. Defects have a strong influence on the electronic, optical, thermal, and mechanical properties of the solids, normally deteriorating their characteristics, but they can also be useful, e.g., for doping of semiconductors or quantum computing. Defects are also present in two-dimensional (2D) materials, which have recently been on the forefront of research in materials science, physics and chemistry. The reduced dimensionality of 2D materials, strongly affects the behavior of native and irradiation-induced defects in these systems, so that many concepts of the physics of defects in bulk systems are not applicable for 2D materials or requirem substantial modifications. The goal of the Seminar is to bring together active researchers in the field to discuss "state of the art" in theory and experiment dealing with the physics of defects in 2D materials. The effects of various imperfections on the properties of 2D systems will be addressed. The attendees will learn about recent developments in the theorectical methods and characterization techniques used to study deffects in 2D materials. Particular attention will be paid to defects in technologically important graphene and transition metal dichalcogenides. The response of 2D materials to ion and electron irradiation will also be addressed.

Scientific Organizers:

Dr. Stefan Facsko	Helmholtz-Zentrum Dresden-Rossendorf, Germany E-mail: s.facsko@hzdr.de
Dr. Arkady Krasheninnikov	Helmholtz-Zentrum Dresden-Rossendorf, Germany E-mail: a.krasheninnikov@hzdr.de
Prof. Dr. Thomas Michely	Universität zu Köln, Germany E-mail: michely@ph2.uni-koeln.de
Prof. Dr. Marika Schleberger	Universität Duisburg-Essen, Duisburg, Germany E-mail: marika.schleberger@uni-due.de

Introduction

Administrative Organization:

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Registration:

Martina Albert and Marion Reisinger
(WE-Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (17:00 h – 21:00 h)
and Monday (08:30 – 13:00 h)

Program

Program

Sunday, 7 May 2023

17:00 – 21:00	Registration
From 18:00	*BUFFET SUPPER and informal get-together*

Monday, 8 May 2023

08:00	*BREAKFAST*	

Chair: Stefan Facsko

09:00 – 09:15	Scientific organizers	**Welcome words**
09:15 – 09:45	Arkady Krasheninnikov	**Introduction:** **What is special about defects in 2D materials?**
09:45 – 10:30	Matthias Batzill	**Excess Metal Induced Defect Formation and Compositional Phase Transformations in 2D Transition Metal Dichalcogenides**
10:30 – 10:50	Herve Aubin	**Hydrogenic Spin-Valley states in Bromine-doped 2H-MoTe2**
10:50 – 11:30	*COFFEE BREAK*	

Chair: Andrey Turchanin

11:30 – 12:15	Kristian Thygesen	**How ab initio calculations can help identifying useful defects for quantum technology**
12:15 – 12:35	Harriet Åhlgren	**Introducing individual metal atoms into graphene**
12:35 – 12:55	Silvan Kretschmer	**Understanding defect production in 2D materials under ion irradiation from advanced first-principles calculations**

Program

Monday, 8 May 2023

13:00 – 14:30	*LUNCH*	

Chair: Matthias Batzill

14:30 – 15:15	Andrey Turchanin	**Influence of intrinsic and extrinsic defects on the electronic and photonic properties of TMD monolayers**
15:15 – 16:00	Alexandra Radenovic	**Nanofluidics-next frontiers with hBN**
16:00 – 16:20	Łukasz Gelczuk	**Native Point Defects in Transition Metal Dichalcogenides - Experimental Verification of Theoretical Prediction**
16:20 – 17:00	*COFFEE BREAK*	
17:00 – 19:15	**NETWORKING**	
19:30	*DINNER*	

Program

Tuesday, 9 May 2023

08:00	*BREAKFAST*	

Chair: Oleg Yazyev

09:00 – 09:45	Steven Louie	**Excitons and Photophysics of 2D Materials: Effects of Defects and Moiré Structures**
09:45 – 10:30	Wouter Jolie	**Correlated quasiparticles in MoS_2 mirror twin boundaries on graphene**
10:30 – 10:50	Christopher Leist	**Deep learning-supported in-situ HRTEM experiments on graphene**
10:50 – 11:30	*COFFEE BREAK*	

Chair: Wouter Jolie

11:30 – 12:15	Oleg Yazyev	**Graphene nanoribbon junctions as elementary components of nanoelectronic circuits**
12:15 – 12:35	Laura Susana	**Atomic scale mapping of the electric field and charge density in BN nanostructures by 4D-STEM**
12:35 – 12:55	Manuel Längle	**Creation of noble gas clusters in a graphene sandwich through low energy ion irradiation**
12:55 – 13:00	**Conference photo** *(in front of the lecture hall)*	
13:00 – 14:30	*LUNCH*	

Program

Tuesday, 9 May 2023

Chair: Richard Wilhelm

14:30 – 15:15	Lino Pereira	**Functionalization of 2D materials using ultralow energy ion implantation**
15:15 – 16:00	Alex Belianinov	**Low Energy Implantation with Focused Ion Beams**
16:00 – 16:20	Mahdi Ghorbani-Asl	**The role of defects and impurities in the formation of crystals between bi-layer graphene upon alkali metal atom intercalation**
16:20 – 17:00	*COFFEE BREAK*	

Chair: Arkady Krasheninnikov

17:00 – 17:45	**Poster flashes 1**
17:45 – 19:15	**Poster session 1**
19:30	*DINNER*

Program

Wednesday, 10 May 2023

08:00	*BREAKFAST*	

Chair: Nasim Alem

09:00 – 09:45	Kazutomo Suenaga	**Electron microscopy and spectroscopy of 2D hybrid materials**
09:45 – 10:30	Jani Kotakoski	**Electron irradiation-induced defects in 2D materials in vacuum and in low-pressure atmospheres**
10:30 – 10:50	Michael Kiarie Kinyanjui	**How do atomic-scale lattice defects modulate ordered electronic phases in 2D quantum materials?**
10:50 – 11:30	*COFFEE BREAK*	

Chair: Jani Kotakoski

11:30 – 12:15	Richard Wilhelm	**Extended defect production in 2D materials by the impact of individual slow highly charged ions**
12:15 – 12:35	Zahra Fekri	**Modification of charge transport in single-layer MoS2**
12:35 – 12:55	Piotr Żemojtel	**First-principles analysis of the point-defects influence on spectroscopic properties of CdSe nanoplatelets**
13:00 – 14:30	*LUNCH*	
14:30 – 18:30	***EXCURSION***	
19:00	***HERAEUS DINNER*** *(social event with cold & warm buffet with complimentary drinks)*	

Program

Thursday, 11 May 2023

08:00	*BREAKFAST*	

Chair: Alex Belianinov

09:00 – 09:45	Hannu-Pekka Komsa	**Simulating Raman spectra of defective 2D materials**
09:45 – 10:30	Marija Drndić	**Sculpting of 2D Materials: From Pores and Nanoporous Membranes**
10:30 – 10:50	Sadegh Ghaderzadeh	**Ab Initio Molecular Dynamics Simulations of Metal-Particles Landing on Pristine and Defective Two-Dimensional Materials in Sputter Deposition Experiments**
10:50 – 11:30	*COFFEE BREAK*	

Chair: Marija Drndić

11:30 – 12:15	Adam Gali	**Defect spins and qubits in hexagonal boron nitride from first principles theory guiding experiments**
12:15 – 12:35	Nasim Alem	**High-resolution S/TEM Imaging and Cathodoluminescence of 2D MoSe2/WSe2 Nanodot/Matrix In-plane Heterostructures**
12:35 – 12:55	Barbara Maria Mayer	**Point defects in monolayer h-BN created by low energy argon irradiation and characterized through scanning transmission electron microscopy**
13:00 – 14:30	*LUNCH*	

Program

Thursday, 11 May 2023

Chair: Bruno Schuler

14:30 – 15:15	Chih-Kang Shih	**Scanning tunneling spectroscopy of van der Waals bilayers - from moire superlattices to moire quasicrystals**
15:15 – 16:00	**NN**	**TBA**
16:00 – 16:20	Maja Groll	**Investigation of the atomic electric field distribution in pristine and defective 2D WSe2 by differential phase contrast STEM**
16:20 – 17:00	*COFFEE BREAK*	

Chair: Arkady Krasheninnikov

17:00 – 17:45	**Poster flashes 2**	
17:45 – 19:15	**Poster session 2**	
19:30	*DINNER*	

Program

Friday, 12 May 2023

08:00	*BREAKFAST*	

Chair: Hannu-Pekka Komsa

09:00 – 09:45	Bruno Schuler	**Single dopants in transition metal dichalcogenides under the scanning probe microscope**
09:45 – 10:30	Sarah Haigh	**Surfaces and Interfaces in Transition Metal Dichalcogenides studied by Advanced Transmission Electron Microscopy**
10:30 – 10:50	Renu Rani	**Single photon emitters in hBN via ultra-low energy helium ion implantation**
10:50 – 11:30	*COFFEE BREAK*	

Chair: Thomas Michely

11:30 – 12:15	Vincent Meunier	**Quantum theory of sputtering rates in 2D materials by transmission electron microscopy**
12:15 – 12:35	Scientific organizers	**Closing remarks & poster awards**
12:35 – 13:30	*LUNCH*	

End of the seminar and departure

NO DINNER for participants leaving on Saturday or Sunday; however, a self-service breakfast will be provided on Saturday, on Sunday self catering!

Posters

Posters 1

Behrouz Arash & Shadab Zakavati	**Atomistically-informed phase-field fracture modeling of defective graphenes**
Alex Armstrong	**A density functional theory investigation into the origin of p-type doping in MoS2 via Ultraviolet-Ozone Treatment**
Laric Bobzien	**An Ultrafast STM Probing the Dynamics at Single Defects in 2D Materials**
Minh Bui	**Optical properties of monolayer MoSe2 irradiated with ultra-low energy Cr ions**
Thuy An Bui	**Creation of single vacancies in hBN with electron irradiation**
Carlos Campos	**Microstructural characterization of highly-disordered nanocrystalline Transition-Metal Chalcogenides prepared by mechanochemical synthesis**
Leon Daniel	**Ion induced defects in two-dimensional tungsten diselenide boron nitride heterostructure**
Francis Davies	**Interface Defect Engineering and Morphological Control of Lateral 2d Heterostructures**
Lysander Huberich	**Charge-dependent symmetry breaking in Rhenium-doped MoS2**
Daniel Jansen	**Local creation of point defects in two-dimensional MoS2**
Wael Joudi	**Correlated AFM/STEM study on the Mechanical Stiffness of Defect-Engineered Graphene**
Osamah Kharsah	**Niobium Doping-Induced Ambipolar Transport in Molybdenum Disulfide for Optoelectronic Devices**
Marko Kriegel	**Competing Processes as Quality Limitation: New Insights into Microscopic Growth Mechanism of Hexagonal Boron Nitride on Ir(111)**
Anand Kumar	**Fabrication and Polarization Dynamics Single Photon Emitters in Hexagonal Boron Nitride**
Prosun Santra	**Effects of tensile strain on the formaiton energy of point defcts in 2D h-BN**

Posters 2

Mitisha Jain	**Electron beam induced chemical etching of 2D materials in the transmission electron microscope**
Vilko Mandić	**The role of the defects in 1D/2D organised charge transfer thin films of the perovskite solar cells**
Alexander Markevich	**Oxygen-mediated defect formation and degradation in 2D MoS2 and MoTe2**
Kalaiarasan Meganathan	**Raman features of gas-phase-grown WS2 monolayer flakes: Influence of precursor molar flow rate on quality**
Hamid Mehdipour	**Structural Defects in Janus MoSSe Monolayer: A Density Functional Theory Study**
Moritz Quincke	**A TEM preparation technique to relate the electronic signature of defects with their atomic structure**
Affan Safeer	**One dimensional Defects in Epitaxially Grown CrS2 Monolayer**
Armin Sahinovc	**Comparison of machine learning strategies in the high-throughput exploration of ABO2 delafossites**
Sebastian Schaper (born Funke)	**Imaging ellispometry for identification and characterziations of 2d-materials**
Pawel Scharoch & Jakub Ziembicki	**Band parameters of group III–V semiconductors in wurtzite structure**
Miguel C. Sequeira	**The influence of the surface on the response of GaN to Strongly Ionising Radiation**
Dedi Sutarma	**Understanding the role of defects in WS-2 layers in contact with ZnO**
Amit Tsipin	**Single Charge Transport through Atomic Defects Embedded in 2D Materials**
Vodeb Vodeb	**Simulating False Vacuum Decays in a Two-Dimensional Mesoscopic Quantum System Using Programmable Quantum Annealing**
Tom Weinert	**Low-Energy Ion Implantation with an Electron Beam Evaporator**

Abstracts of Lectures

(in alphabetical order)

Introducing individual metal atoms into graphene

A. Trentino[1], K. Mizohata[2], G. Zagler[1], M. Längle[1], K. Mustonen[1], T. Susi[1], J. Kotakoski[1] and E. H. Åhlgren[1]

[1]University of Vienna, Vienna, Austria
[2] University of Helsinki, Helsinki, Finland

Heteroatoms embedded in 2D materials show promising properties. Dopants from the transition metals group have been studied for their role in functionalising 2D materials from single atom catalysis to tailoring their electronic, optical and magnetic properties as well as quantum topology. Low energy ion implantation offers an accurate and controllable way of introducing atoms into the two dimensional structure. The method benefits from scalability and existing facilities are widely used in the semiconductor industry. We study single Au atoms in freestanding monolayer graphene. Au dopants are implanted into substitutional sites in graphene double vacancies using ultra low implantation energies. By combining two Au energies in a consecutive manner, first 200 eV to introduce double vacancies in the lattice and then 25 eV to implant the Au, the process results in covalently bound individual Au atoms within the graphene lattice, see Figure 1. This ensures that the inefficient momentum transfer that stems from the large mass difference between the projectile and the target atoms is overcome.

High resolution aberration corrected scanning transmission electron microscopy of the resulting structures reveals a multitude of single Au atoms in four-fold configurations embedded in the lattice [1]. The distinct brightness of the Au substitutes compared to the surrounding carbon atoms makes them easily visible during imaging. The heteroatoms are stable under electron beam irradiation at 60 kV. Electron energy loss spectroscopy at the dopant site confirms the composition of the substitutes. The low loss energy range does not indicate broadening of the pi and pi + sigma surface plasmon modes as seen locally with Si dopants.

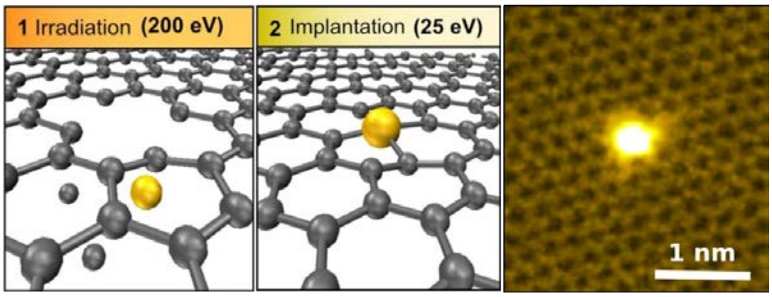

Figure 1: Implantation with two consecutive energies results in individual Au atoms within the graphene lattice.

References

[1] A. Trentino et al. 2D Materials **9**, 025011 (2022)

High-resolution S/TEM Imaging and Cathodoluminescence of 2D MoSe2/WSe2 Nanodot/Matrix In-plane Heterostructures

Saiphaneendra Bachu[1], Steffi Woo[2], Benjamin Huet [1, 3], Nicholas Trainor[1], Joan M Redwing[1, 3], Mathieu Kociak[2], Luiz HG Tizei[2], Nasim Alem[1, 3,]

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[2]Laboratoire de Physique des Solides, Université Paris-Saclay, CNRS-UMR 8502, Orsay, 91405, France
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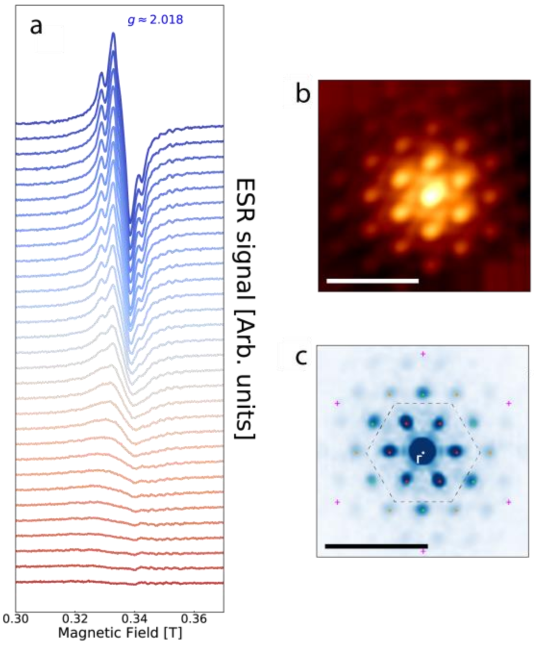
Recent progress in scanning/transmission electron microscope (STEM) imaging and spectroscopy techniques have enabled significant insight into the local atomic and electronic structure of nanomaterials as well as their nano-optical response. The unprecedented spatial resolution of the STEM, in combination with Electron energy loss spectroscopy (EELS) and Cathodoluminescence (CL) techniques has enabled us to detect the spatial variations in the absorption and emission characteristics of materials at the nanoscale regime and correlate them with the local structure and chemistry at the same time and location. Furthermore, recent advancements in data-driven analysis and machine learning (ML) algorithms has enabled us to extract meaningful information from large data sets and to separate various signals spectrally and spatially, without prior knowledge. In this talk, we will present our recent study on the light emission characteristics in two-dimensional (2D) transition metal dichalcogenide (TMD) quantum dot $MoSe_2$/WSe_2 in-plane heterostructure films, with $MoSe_2$ nanodots ranging from below 10 nm to about 100 nm, embedded in WSe_2 matrix. Using CL and in combination with high resolution STEM imaging and EELS, this study explores the localized light emission signatures from the MoSe2 nanodots and WSe2 matrix as a function of their size and atomic structure. With the application of unsupervised ML based algorithms to analyze the CL datasets, this study uncovers excitons from the nanodots, matrix, and the interface, and their emission characteristics are further discussed.

Hydrogenic Spin-Valley states in Bromine-doped 2H-MoTe$_2$

V. Sheina[1], G. Lang[2], V. Stolyarov[3], S. Marchenkov[4], S. Naumov[4], A. Perevalova[4], J.C. Girard[1], G. Rodary[1], C. David[1], L.R. Sop[1], D. Pierucci[1], A. Ouerghi[1], J.L. Cantin[5], B. Leridon[2], M. Ghorbani-Asl[6], A.V. Krasheninnikov[6], H. Aubin[1]

[1] Centre de Nanosciences et de Nanotechnologies, Université Paris-Saclay, France
[2] Laboratoire de Physique et d'Étude des Matériaux, ESPCI, Paris, France
[3] MIPT, Moscow, Russia
[4] M.N. Mikheev Institute of Metal Physics, Ekaterinburg, Russia.
[5] INSP, Sorbonne-universités, Paris, France
[6] Institute of Ion Beam Physics and Materials Research, Dresden, Germany

In semiconductors, the identification of doping atomic elements allowing to encode a qubit within spin states is of intense interest for quantum technologies. In transition metal dichalcogenides semiconductors, the strong spin-orbit coupling produces locked spin-valley states with expected long coherence time. I will present a study of substitutional Bromine Br_{Te} dopant in 2H-MoTe$_2$. Electron spin resonance measurements, shown in Fig.**a**, indicates that this dopant carries a spin with long-lived nanoseconds coherence time. Using scanning tunneling spectroscopy, we find that the hydrogenic wavefunctions associated with the dopant levels have characteristics spatial modulations, shown in Fig.**b**, that result from their hybridization to the Q-valleys of the conduction band. From a Fourier analysis of the conductance maps, shown in Fig.**c**, we find that the amplitude and phase of the Fourier components change with energy according to the different irreducible representations of the impurity-site point-group symmetry. These results demonstrate that a dopant can inherit the locked spin-valley properties of the semiconductor and so exhibit long spin-coherence time.



Paper under review.

Excess Metal Induced Defect Formation and Compositional Phase Transformations in 2D Transition Metal Dichalcogenides

M. Batzill

Department of Physics, University of South Florida, Tampa, USA

The reduced structural constraints in 2D materials enable the incorporation of excess atoms into the 2D-lattice. These excess metals may result in point or extended defects or transformation into new stoichiometric phases. In this talk we discuss different mechanisms to induce compositional variations by reacting transition metal dichalcogenides (TMDs) with metal atoms or by removing chalcogen atoms. Not surprisingly, given the broad nature of the transition metal dichalcogenides, different transition metal groups respond differently to metal rich conditions. The early transition metal dichalcogenides (group 5 transition metals) have a preference to insert excess metals in between TMD layers [1,2]. Group 6 TMDs may incorporate elements at interstitial sites which may cause restructuring into metal-rich mirror twin grain boundary networks [3,4]. While the group 10 $PtTe_2$ can transform into a different stoichiometric phase, i.e., 2D Pt-monotelluride [5,6,7]. Understanding the processes by which TMDs react with excess metals shine light on synthesis processes and point towards methods for modifying 2D materials and induce new functionalities.

References

[1] M. Bonilla, et al. Adv. Mater. Interf. **7**, 2000497 (2020)
[2] K. Lasek, et al. ACS Nano **14**, 8473 (2020)
[3] P.M. Coehlo, et al. ACS Nano **12**, 3975 (2018)
[4] V. Pathirage, et al. Mater. Today Nano **in press**
[5] J. Li, et al. Chem. Mater. **33**, 8018-8027(2021)
[6] K. Lasek, et al. ACS Nano **16**,9908 (2022)
[7] K. Lasek, et al. Nano Letters **22**, 9571 (2022)

Low Energy Implantation with Focused Ion Beams

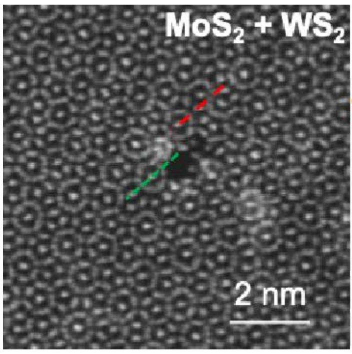
Michael Titze[1], Chris Smyth[1], Jonathan D. Poplawsky[2], Barney Doyle[1], Edward Bielejec[1], Alex Belianinov[1]

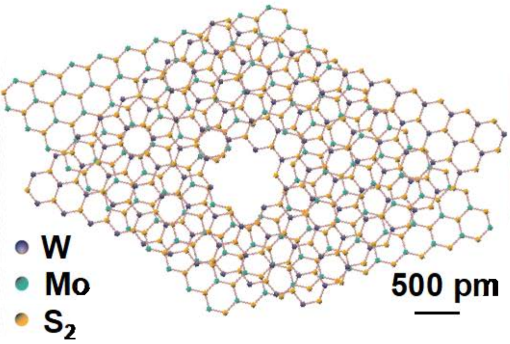
1. *Ion Beam Laboratory, Sandia National Laboratories, Albuquerque New Mexico, 87185*
2. *Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge TN, 37831*

Ion implantation is a key capability for the semiconductor industry. As devices shrink, novel materials enter the manufacturing line, and quantum technologies transition to being more mainstream, traditional implantation methods fall short in terms of energy, ion species, and positional precision. However, lowering the implantation energy while maintaining nanometer scale spot size is a technological challenge. This presentation will show an overview of techniques at Sandia National Laboratories Ion Beam Facility that allow focused ion implants 35-200 keV range for quantum relevant applications.

Additionally new developments in sub-2 keV focused ion implants into Si and 2D devices, using a focused ion beam system, validated by atom probe tomography will be shown. We illustrate that identical results for low energy ion implants can be achieved by either lowering the column voltage, or decelerating ions using bias – while maintaining good spatial resolution. Furthermore, our data reveal that standard implant modeling approaches overestimates experimental depth by a significant margin. Finally, we discuss how our results pave a way to much lower implantation energies, while maintaining high spatial resolution.

Sculpting of 2D Materials:
From Pores and Nanoporous Membranes





Marija Drndic

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Introducing atomic-scale holes in 2D materials changes their electrical and optical properties. When 2D materials are suspended, vacancies make the membranes permeable to ions and molecules in liquid or gas phases, allowing transport studies at atomic scales. Angstrom-size holes allow the passage of water molecules but block the larger hydrated salt ions and can effectively desalinate water. Raman peak shifts combined with TEM, provide a comprehensive approach to characterize the holes and transport through them. When molecules are driven through 2D nanopores in solution, they can perturb the ion current flow through the pore, from which molecule's physical and chemical properties can be inferred. DNA other biomolecules can be detected in this way. Thanks to advanced materials, device designs and custom electronics, the temporal and spatial resolution for their detection has been rapidly improving.

Modification of charge transport in single-layer MoS_2

Abstract

The ability to alter properties of 2D materials through defects engineering can open a new window in the device performance improvements as well as quantum electronics and photonics. Ion beam Irradiation is a controllable technique to modify the electrical and optical properties of 2D materials by defect creation. In this work, we used 5 - 7.5 keV helium and neon ions to modify charge transport in monolayer molybdenum disulfide (MoS_2). Electrical characterization was performed in-situ immediately after ion beam irradiation. Raman and photoluminescence spectroscopy were implemented to characterize optically the effect of ion irradiation on monolayer MoS_2. Our experiments demonstrate that the electrical properties of MoS_2 strongly depend on the nature of the substrate and the ion beam used. Although 10^{12}- 10^{13} helium ions/cm^2 contributes to an increase in the current level, the same range of neon ions deteriorate the channel current. In addition, using hexagonal boron nitride (hBN) between MoS_2 flake and SiO_2 substrate resulted in a different electrical behavior compared to the MoS_2 samples which were directly placed on SiO_2.

Authors

Zahra Fekri1, Phanish Chava1-2, Gregor Hlawacek1, Vivek Koladi1, Tommaso Venanzi1-2, Wajid Awan1, Antony George3, Andrey Turchanin3, Kenji Watanabe4, Takashi Taniguchi4, Manfred Helm1-2, Artur Erbe1-2

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Defect spins and qubits in hexagonal boron nitride from first principles theory guiding experiments

Song Li[1], Anton Pershin[1,2], Péter Udvarhelyi[1,2], Viktor Ivády[3], Ádám Gali[1,2]

[1]*Wigner Research Centre for Physics, Budapest, Hungary*
[2]*Budapest University of Technology and Economics, Budapest, Hungary*
[3]*Eötvös Loránd Science University, Budapest, Hungary*

We have recently developed first principles techniques for theoretical microscopy and spin control of point defects in semiconductors and insulators. We have applied these techniques to several point defects in hexagonal boron nitride (hBN) that are relevant in real hBN materials. We proposed to apply the negatively charged boron-vacancy to realize qubits. This center was indeed later observed in experiments. We have recently simulated the coherence time and Rabi-oscillation of this center with showing an entanglement between the electron spin and the first four neighbor 14N spins. We have recently identified the coupling of the electric field and the strain to the electron spin in the ground state of the center with quantifying the theoretical sensitivity limits and interpreting the optically detected magnetic resonance (ODMR) spectrum of ensembles. We identified an oxygen-related electron paramagnetic resonance center in hBN which produces 2-eV emission with relatively small phonon sideband. Furthermore, we proposed two types of ultraviolet (UV) emitters in hBN: (i) the 5-7 Stone-Wales defects and (ii) the carbon-pair defect structures with the most stable form of a carbon ring. We shall show how the properties of the UV emitters change upon stacking sequences of hBN layers.

This work was supported by the National Research, Development, and Innovation Office of Hungary (NKFIH) grant No. KKP129866 of the National Excellence Program of Quantum-coherent materials project and the Quantum Information National Laboratory supported by the Cultural and Innovation Ministry of Hungary (Grant No. 2022-2.1.1-NL-2022-00004).

Native Point Defects in Transition Metal Dichalcogenides - Experimental Verification of Theoretical Prediction

<u>Ł. Gelczuk</u>[1], J.Y. Kim[2], M.P. Polak[2], I. Szlufarska[2] and R. Kudrawiec[1]

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We present experimental and theoretical studies of native point defects in MX_2 (M = Mo or W; X = S, Se, or Te) transition metal dichalcogenides (TMDs). The deep-level defects were revealed and their charge transition levels were measured by means of deep level transient spectroscopy (DLTS). The DLTS results agreed well with the state-of-the-art computational predictions, made by density functional theory (DFT), using the optimized functional, electrostatic correction, and band alignment. The very good agreement of experimental and computational results validated the computational approach and allowed for identification of the origin of experientially found defect levels. We found that the chalcogen vacancy is the most stable defect in bulk MX_2, which creates the 0/−1 charge transition inside the band gap and that the selection of transition metal has only little effect on the position of the 0/−1 charge transition. Verified DFT approach has been then used to calculate the charge transition levels of defects in monolayer 2D MX_2, which are experimentally challenging to be measured directly by DLTS. This is because of their atomic-scale thickness, which excludes the existence of a sufficient width of the depletion region to be modulated by voltage pulses through the vertical Schottky diode or p-n junction during measurements. By comparing the bulk and 2D TMDs data, we find that reduction of dimensionality of TMDs to 2D has a significant impact on defect properties, their formation energies and chemical trends of their charge transition levels. For example, unlike the bulk systems where the metal vacancies have many transition levels inside the band gap, in the 2D systems the metal vacancies create only a single transition level inside the band gap. This finding may explain observed differences in optical properties of 2D TMDs synthesized with different methods and lays foundation for future developments of more efficient TMD-based applications.

Ab Initio Molecular Dynamics Simulations of Metal-Particles Landing on Pristine and Defective Two-Dimensional Materials in Sputter Deposition Experiments

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Magnetron sputtering is a physical vapour deposition process used to produce high quality thin coatings at an industrial scale. Recently, this technique has emerged as an effective tool for metal nanocluster fabrication for catalysis [1] and utilisation in electronic devices and batteries. Metal sputter deposition involves ejecting metal atoms from a target through collisions with energetic ions of plasma (typically, that of an inert gas) created near the target surface. The ejected metal atoms and small nanoclusters can be deposited on a wide range of support materials suitable for a given application.

Atomic-scale processes underpinning atom/nanocluster deposition on the support are yet to be fully characterised and understood. An accurate study of the complex metal-substrate interactions can be achieved by ab-initio molecular dynamics (AIMD). In this study, we carry out AIMD simulations, as well as density functional theory (DFT) calculations, to investigate the interactions of various metal atoms with two-dimensional (2D) h-BN and graphene sheets.

Our results show that defects in 2D systems play a crucial role in clusterisation of metal atoms on the surface, which determines the metal surface area available for catalysis. Furthermore, our simulations of metal-cluster dynamics on defective 2D sheets support the experimental observations on temperature-dependence of metal clusterisation/dispersion on the substrate. Finally, we provide quantitative estimates of the tuning parameters in the magnetron sputtering experiments to engineer defects prior to the metal deposition. The results of our calculations can be directly used to guide metal-deposition experiments to tune the catalytic activities of the metal-coated 2D surfaces.

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The role of defects and impurities in the formation of crystals between bi-layer graphene upon alkali metal atom intercalation

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The formation of quasi-two-dimensional crystals containing multiple Li layers was reported inside bilayer graphene using in-situ transmission electron microscopy and further investigated for other two-dimensional materials.[1,2] Later experiments demonstrated that Li crystals nucleate mainly at defect sites of graphene and the de-lithiation process is heavily influenced by impurities, such as oxygen impeding the lithiation/de-lithiation cycles. Using state-of-the-art first-principles calculations, we systematically study the interaction of alkali metal (Li and Na) atoms and those in FCC crystals with vacancy-type defects in graphene. Our results demonstrate that quasi-2D Li crystals encapsulated between graphene sheets nucleate at the defects and that the interaction of not only isolated Li atoms, but also Li crystals with the defects in graphene is strong.[3] Similarly, point defects facilitate Na adsorption in graphene whereas the interaction of Na atoms with pristine graphene is not energetically favorable. We investigate the behavior of impurity atoms most likely to be found in the encapsulated Li crystals, such as O, N, S and F. Our calculations indicate that all impurity atoms take octahedral interstitial positions and strongly interact with atoms in Li crystals, thus impeding the de-lithiation process. It is also found that the presence of lithium atoms may lead to a drop in vacancy formation energy in graphene due to energy gain from the formation of lithium carbide molecules. Our findings can help rationalize the results of in-situ TEM experiments and shed light on the role of impurities in the degradation of anode materials.

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Investigation of the atomic electric field distribution in pristine and defective 2D WSe2 by Differential Phase Contrast STEM

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Transition metal dichalcogenides (TMDs) are promising candidates for future optoelectronic devices especially due to their layer-thickness dependent optoelectronic properties, such as a direct band gap for a TMD monolayer instead of an indirect band gap for the bulk material[1]. In addition, the layered structure facilitates a comparably easy fabrication of 2D thin films. The optoelectronic properties of these films are dominated by the electronic structure of the individual layers and influenced by the electric field distribution around single atoms and defects[2]. Therefore, investigation of the electric field and charge density distribution with sub-atomic resolution is crucial. One technique which allows for the characterization of electric fields within a specimen is differential phase contrast (DPC) imaging in scanning transmission electron microscopy (STEM). In combination with state-of-the-art correction of lens aberrations, DPC-STEM even enables to visualize and quantify atomic electric fields[3]. This technique is based on the detection of the centre of mass (CoM) shift of the intensity distribution caused by the Coulomb interaction of the incident electron beam with the electric fields inside the specimen.

We investigated the atomic electric field and charge density distribution of mechanically exfoliated 2D WSe_2 flakes. STEM-DPC measurements are performed with an eight-fold segmented detector and at an acceleration voltage of 80 kV. We reveal the electric field and charge density distribution of 2D WSe_2 flakes with sub-atomic resolution and compare our results with corresponding multislice image simulations. For a WSe_2-trilayer, we measure and visualize the characteristic electric field distribution in the vicinity of a single point defect by comparison of DPC-STEM images of a pristine and a defective 2D lattice.

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Surfaces and Interfaces in Transition Metal Dichalcogenides studied by Advanced Transmission Electron Microscopy

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Surfaces and interfaces are key to the performance of 2D materials and their heterostructures including for new optoelectronic phenomena [1], modifying and enhancing electron interactions in moire superlattices [2], nanofluidics to study molecular or ionic transport [3]. The impressive progress being achieved in the field crucially depends on knowledge of the atomic structure of these systems, which in many cases can only be analysed by transmission electron microscopy (TEM) techniques. In this talk I will present our scanning TEM (STEM) investigations of unusual lattice reconstruction that occurs at the interfaces in twisted transition metal dicholcogenide bilayers [4]. Complementary scanning tunnelling measurements show that such reconstruction creates strong piezoelectric textures, which can be engineered by the application of applied field in the electron microscope [5]. This talk will also illustrate how we can use 2D heterostructures to produce a new design of in-situ liquid cell for the TEM [6,7]. This approach overcomes limitations of conventional silicon nitride window membranes allows atomic resolution imaging of adatom dynamics at solid-liquid interfaces [7]. We further show how a suite of (4D) STEM imaging and spectroscopy methods can be used to probe deintercalation processes at the nanoscale and how these evolve as a function of time and annealing temperature [8].

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Correlated quasiparticles in MoS_2 mirror twin boundaries on graphene

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Electrons are prone to strong correlations when confined into one-dimensional (1D) cavities. An ideal experimental testbed for the observation of correlated electronic behavior is found in mirror twin boundaries (MTBs) of the two-dimensional material MoS_2. These MTBs function as structurally perfect 1D cavities, are only weakly coupled to the environment and accessible to spatially resolved spectroscopic investigations using scanning tunneling microscopy.

In my talk I will show that the confined quasiparticles within finite MoS_2 MTBs transform into spin and charge modes as described by the Tomonaga Luttinger theory of strongly interacting 1D electrons [1]. In addition, a Kondo resonance, delocalized over the entire length of the MTB, emerges when the highest occupied mode is half filled [2]. The unique construction of our Kondo system enables us to directly measure the energies of both the Kondo resonance and the half-filled confined level, as well as their correlated beating along the boundary. Thus, our experimental Kondo system, in conjunction with numerical renormalization group (NRG) calculations, enables us to test the predictive power of the Anderson model which is the basis of the microscopic understanding of Kondo physics.

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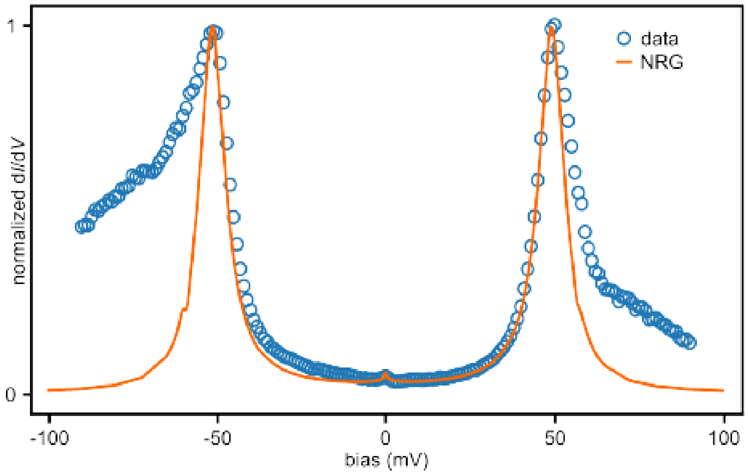

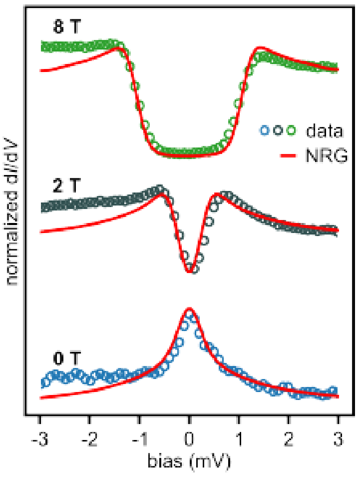

How do atomic-scale lattice defects modulate ordered electronic phases in 2D quantum materials?

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Some 2D quantum materials display a complex interplay of various electronic phases. [1] These include stripe-phases, spin-density waves, superconductivity, charge-density waves (CDW), charge-ordering among others. Due to coupling of electronic and lattice degrees of freedom, some of these electronic phases are very sensitive to lattice defects introduced in the underlying atomic lattice through external perturbations such as strain, intercalation, pressure, irradiation among others.
One consequence is often spatial electronic phase separation and development of phase defects as well as disorder in the electronic phases. This interplay results in a complex landscape of ordered electronic phenomena, defects in both atomic lattice and electronic phase and disorder. Understanding the nature of the interaction calls for development of spatially resolved probes and methods sensitive to both lattice defects and ordered electronic phases
To investigate this issue, we have used (i) 2D layers with a well-defined CDW state (ii) induced lattice defects in these layers through hydrostatic pressure and molecular intercalation (iii) imaged the atomic scale response of the CDW electronic phase to these lattice defects. [2], [3] We find that the CDW electronic phase responds with an elastic-like strain response to the lattice defects and deformations induced in the underlying atomic lattice. This is characterized by phase defects in the CDW electronic phase including dislocations and domain walls. Our results show the role of externally induced lattice deformations and defects in modulating, stabilizing or disordering electronic phases in 2D quantum materials.

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Simulating Raman spectra of defective 2D materials

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Raman spectroscopy is a widely-used non-destructive materials characterization technique, that is also indispensable in the study of 2D materials. It is used to gain insight to both material identity and its quality affected e.g., by strain, doping, defects, etc. For interpreting the spectra and associated changes, it is beneficial to compare them to spectra simulated using first-principles methods. Raman scattering arises from the change of polarizability (or electronic susceptibility or dielectric constant) with the atomic vibrations. In large systems, calculating the polarizability upon the displacement of each atom or each phonon mode becomes computationally prohibitively expensive. This can be circumvented by using polarizability models, whose construction can be guided by physical intuition or relying on machine-learning methods. Furthermore, when combined with machine-learning force fields, these models allow one to carry simulations for very large systems and spanning long time scales.

In my talk, I will first introduce and compare few polarizability models, from physics-based to machine-learning ones, and describe how to simulate the spectra while also including the effects of temperature, anharmonicity, disorder, etc. To illustrate the kind of information that can be extracted from these simulations, I will then show a few examples from our recent work, where we have successfully applied the methods to defective MoS_2 [1,2,3], 2D material alloys [1,4], SnS multilayer flakes [5], 2D MXenes with a random distribution of surface functional groups [6], as well as complex bulk materials such as perovskites.

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Electron irradiation-induced defects in 2D materials in vacuum and in low-pressure atmospheres

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It is known since decades, that electron irradiation leads to damage in materials during imaging in (scanning) transmission electron microscopy. In materials prone to ionization or electronic excitations this is known to be largely due to inelastic electron scattering, whereas in conductive materials the main damage mechanism is knock-on damage caused by elastic electron scattering. However, it only became possible recently with the advent of aberration corrected microscopes and 2D materials to quantify the damage in detail. It was confirmed, that in graphene which is an excellent conductor, the observed atomic scale damage could indeed be explained via simple knock-on events [1]. However, it became in the meanwhile also obvious that the residual vacuum in the microscope column can in some cases play an important role in the damage creation. For graphene, this has been shown to only play a role at point defects and edges [2], whereas for oxygen sensitive 2D materials, such as $MoTe_2$, it also influences areas with no defects [3]. In contrast to graphene, in semiconducting 2D materials such as MoS_2 (for which the residual vacuum does not play a significant role [3]) it has recently been proposed [4] that the atomic-scale process underlying electron irradiation-induced damage arises from a combination of inelastic and elastic scattering, where the same electron first locally excites the electronic structure and at the same time scatters elastically from a nucleus in the material causing its displacement. It appears that this process can alternatively be explained either through impact ionization or direct valence excitation [5], but additional experimental data and further developed theoretical models are sorely needed to provide the final explanation.

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Understanding defect production in 2D materials under ion irradiation from advanced first-principles calculations

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Defects have a major influence on the properties of 2D materials, as they essentially consist of surface-only. Contrary to what word “defect” implies, defects can have not only detrimental effects on the material properties, but are often introduced to tune the magnetic, electronic and optical response of the system. The number of defects produced by electron and ion irradiation can be assessed using first-principles calculations [1-3]. Here, we report on our recent work where using ab-initio molecular dynamics we calculated the probability to form defects of different types in various 2D materials including MoS_2 and graphene on Cu(111) substrate under low-energy ion irradiation. We further study the neutralization and deexcitation of single-charged ions upon transmission through graphene and 2D MoS_2 by means of non-adiabatic Ehrenfest dynamics to demonstrate the potential of this powerful simulation technique.

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Creation of noble gas clusters in a graphene sandwich through low energy ion irradiation

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Due to their chemical inertness, noble gases do not condense under normal conditions. When trapped between two graphene sheets, however, the atoms are forced together by the external pressure that leads to the formation of clusters [1]. We create such clusters by implanting singly charged low energy (< 30 eV) ions into suspended bi- and double layer graphene, which allows their direct imaging through (scanning) transmission electron microscopy inside the graphene sandwich [2].
So far the implantation parameters of Ar, Kr and Xe into doublelayer graphene have been experimentally determined. In our work we look at the implanted atoms, their cluster formation, stability and phase.
The encapsulated clusters show dynamical behavior such as "jumps" between different positions. Using molecular dynamics simulations we are able to understand the jumping behavior between specific positions. The trapped clusters also show interesting phase behavior. While all small clusters remain solid, larger clusters exhibit either solid- or liquid-like structures depending on their size, chemical element and possibly local microscopic environment.

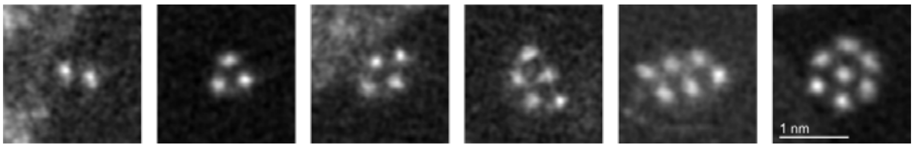

Figure 1: Filtered annular dark field scanning transmission electron microscopy images of Xe clusters to up to seven atoms.

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Deep learning-supported in-situ HRTEM experiments on graphene

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Atomic-resolution in situ electron microscopy provides a huge number of parameters that allow new insights into dynamical behavior of ultra-thin materials. We perform in-situ experiments with graphene and polymeric carbon materials as well as with metal atom clusters on graphene using our Cc/Cs-corrected SALVE (Sub-Angstrom Low-Voltage Electron Microscopy) instrument. Due to the fast dynamics of carbon atoms in graphene and metal atoms forming clusters on graphene under electron bombardment, an immense amount of data is generated both in terms of the number of frames acquired and the amount of information per frame. Just as an example, in a 10 nm × 10 nm image, the trajectories of more than 4000 carbon atoms must already be described. This makes the manual evaluation and the application of conventional image analysis methods, such as by hand-made filter kernels, untenable due to their enormous time consumption and the possibility of user bias.

Deep learning in the form of convolutional neural networks (NN) offers a reliable and effective way to handle large amounts of complex image data. Using simulated training data results in a flexible training pipeline that is robust to user bias. By coupling multiple networks, we have incorporated multi-tasking capability into the workflow, including segmentation of multilayers, contaminants, and micropores and subtraction of non-uniform illumination intensity. To further investigate the generality of our deep learning pipeline, the robustness of the NN was demonstrated on various tasks in different sample systems, including identification of defects and dopants in graphene, shape and positions detection of adsorbed metal clusters, and statistical analysis of amorphous polymeric carbon membrane. By the application of carefully trained neural networks, it becomes possible to fully exploit the richness of data captured in TEM images.

Excitons and Photophysics of 2D Materials: Effects of Defects and Moiré Structures

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Defects and environmental modifications can greatly change the photophysics of atomically thin two-dimensional (2D) materials. In this talk, I present several interesting phenomena related to point defects as well as moiré physics on the optical properties of 2D materials using *ab initio* GW-BSE theory. We study the effects of chalcogen vacancies on the optical properties of monolayer transition metal dichalcogenides (TMDs). The defect states give rise to strongly bound defect excitons and hybridize with excitons of the pristine system, reducing the valley-selective circular dichroism in TMDs which suggests a pathway to tune spin-valley polarization through defects. For moiré TMD bilayer systems, we discover a rich diversity of excitonic states depending sensitively on twisted angles. In rotationally aligned WSe_2/WS_2 moiré superlattice, we find some excitons of a modulated Wannier character and others of a previously unidentified intralayer charge-transfer character. In 57.7° twisted bilayer WS_2, we discover layer-hybridized excitons with in-plane charge transfer character. Many of the theoretical predictions have been confirmed by experiments. In another study, our computed results showed that the recent cathodoluminescence experimental finding of on-demand activation and control of color-center emission at the twisted interface of two hexagonal boron nitride flakes is correlated to nitrogen vacancies. The tunable brightness of the emission is related to a twist-induced moiré potential that facilitates electron-hole recombination.

Point defects in monolayer h-BN created by low energy argon irradiation and characterized through scanning transmission electron microscopy

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h-BN monolayer is a 2D material and ultraviolet light emitter. Its point defects can serve as single photon emitters at the mid-infrared-range at room temperature. Therefore, h-BN has a great potential for applications in quantum information processing [1]. However, this is currently impeded due to a lack of knowledge in the effects and manufacturing of point defects [2].

In our work we create defects in h-BN using low energy ion irradiation. The irradiated sample is imaged before and after the irradiation to characterize the resulting defects. The data is acquired semi-automatically with the NionUltraSTEM 100. Automated image acquisition helps to record statistically significant amounts of data. A convolutional neural network is used to characterize the images regarding type and prevalence of the occurring defects.

The distribution of defects before and after the irradiation are approximately the same- however, the defect concentration after the irradiation is ~10 times higher than before exposing it to argon atoms.

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Quantum theory of sputtering rates in 2D materials by transmission electron microscopy.

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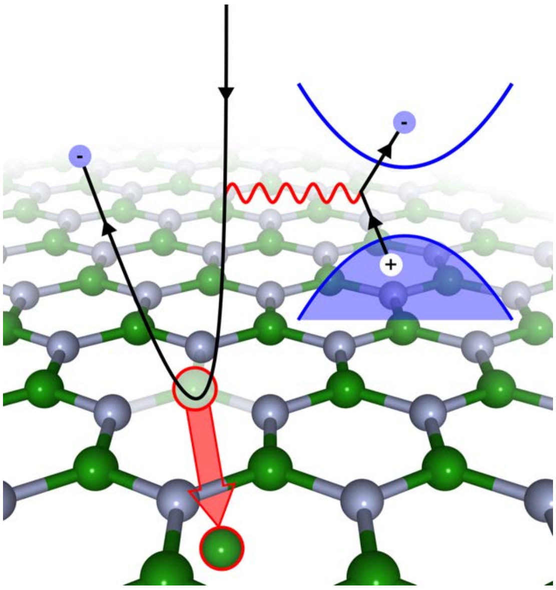
Many computational models have been developed to predict the rates of atomic displacements in two-dimensional (2D) materials under electron beam irradiation. However, these models often drastically underestimate the displacement rates in 2D insulators, in which beam-induced electronic excitations can reduce the binding energies of the irradiated atoms. This bond softening leads to a qualitative disagreement between theory and experiment, in that substantial sputtering is experimentally observed at beam energies deemed far too small to drive atomic dislocation by many current models. To address these theoretical shortcomings, this paper develops a first-principles method to calculate the probability of beam-induced electronic excitations by coupling quantum electrodynamics (QED) scattering amplitudes to density functional theory (DFT) single-particle orbitals. The presented theory then explicitly considers the effect of these electronic excitations on the sputtering cross section. Applying this method to 2D hexagonal BN and MoS_2 significantly increases their calculated sputtering cross sections and correctly yields appreciable sputtering rates at beam energies previously predicted to leave the crystals intact. The proposed QED-DFT approach can be easily extended to describe a rich variety of beam-driven phenomena in any crystalline material. [1]



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Functionalization of 2D materials using ultralow energy ion implantation

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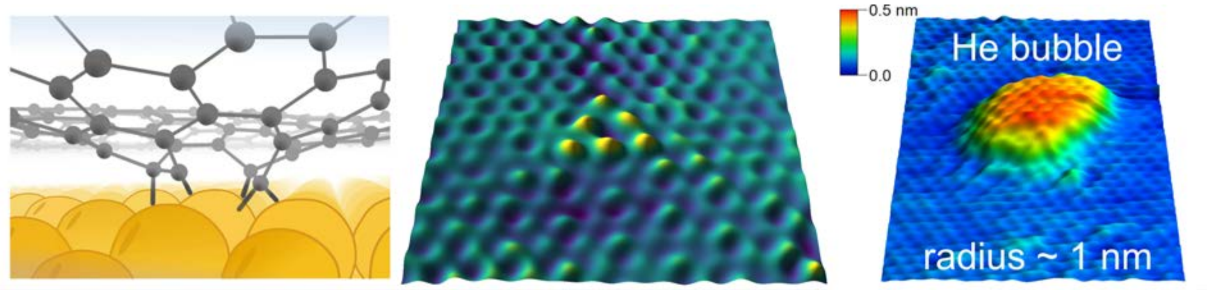
Functionalization of 2D materials generally requires the modification of their physicochemical properties. Several approaches have been explored: the use of different substrates, creation of intrinsic defects (e.g. vacancies), adsorption and intercalation (of atoms, clusters or molecules), substitutional doping, among others. For incorporation of substitutional or intercalated elements, despite the numerous approaches that have been investigated, a major challenge remains: the limited control over the concentration and form of incorporation. An alternative approach is to incorporate the foreign species by ultralow energy (ULE) ion implantation, precisely tuning the number of implanted ions and their kinetic energy. In this talk, I review our recent work on ULE ion implantation of 2D materials, in particular: substitutional doping of graphene [1]; formation of nanobubbles in graphene [2]; formation of bond defects in graphene [3]. Our approach is based on a wide range of characterization techniques (structural and electronic), including scanning tunneling microscopy and spectroscopy (STM/STS), synchrotron-based X-ray photoelectron spectroscopy (XPS), angle-resolved photoemission spectroscopy (ARPES), X-ray magnetic circular dichroism (XMCD), transport measurements, among others. These experimental studies are complemented by density functional theory (DFT) and molecular dynamics (MD) simulations.



Left: Snapshot of MD simulations after ion impact depicting the bond defects formed when the C-C sp2 bonds (gray) are broken and the displaced C atoms (black) form new bonds with the Pt surface (orange). *Center*: STM topography of substitutional manganese in graphene on Cu(111). *Right*: STM topography of helium nanobubble in graphene on Pt(111).

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Nanofluidics-next frontiers with hBN

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In this talk, I will introduce a novel method based on liquid-activated quantum emission from native hBN defects for nanofluidic sensing. Liquids confined down to the atomic scale can show radically new properties. However, only indirect and ensemble measurements operate in such extreme confinement, calling for novel optical approaches enabling direct imaging at the molecular level. Using our method, we harness quantum emission originating from native defects in hexagonal boron nitride (hBN) for molecular imaging and sensing in nanometrically confined liquids. We show that defect activation occurs through chemisorption of organic solvent molecules, revealing single-molecule dynamics at the interface through spatially correlated activation of neighboring defects. Defect emission spectra further offer a direct readout of local dielectric properties, unveiling increasing dielectric order under nanometer-scale confinement. Liquid-activated native hBN defects bridge the gap between solid-state nanophotonics and nanofluidics, opening new avenues for nanoscale sensing and optofluidics.

https://arxiv.org/abs/2204.06287

Single photon emitters in hBN via ultra-low energy helium ion implantation

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A discovery of quantum emitters in hexagonal boron nitride (hBN) has recently incited immense interest for quantum technologies. It offers a platform for fundamental science but is of interest for applications in quantum photonics owing to its robust single photon emission at room temperature. Recent studies have suggested that these SPEs are associated with intrinsic defects, which led to efforts to engineer the SPE in hBN by various methods such as plasma treatment, annealing, laser, e-beam and ion irradiation methods. Despite these efforts, the origin of single photon emission and the correlation of emission with particular defects still need to be scrutinized. Here we use ultra-low energy ion implantation to introduce defects in hBN. We show that helium ions with energies as low as 50 eV are extremely efficient in introducing single photon emitters in hBN. We also show that low temperature annealing increases the density of the emitters. We consider the possible defects that helium ions at the implantation energy can generate in hBN and use statistical data on single photon emitters to discuss the possible origin of the emission. Finally, we discuss the viability of creating emitters in pre-selected locations.

Single Dopants in Transition Metal Dichalcogenides under the Scanning Probe Microscope

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Two-dimensional (2D) semiconductors provide an exciting platform to engineer atomic quantum states in a robust, yet tunable solid-state system. In this talk, I will present our efforts to unravel the interesting physics behind single dopant atoms in transition metal dichalcogenide (TMD) monolayers by means of high-resolution scanning probe microscopy [1-8].

Our recent research on transition metal doped TMDs such as (n-type) Re-doped MoS_2 and (p-type) V-doped WSe_2 reveals the significance of the charge state in the spectroscopic signature of these defects. By substrate chemical gating, we can stabilize three charge states of Re_{Mo}, where two of the charge states exhibit symmetry broken electronic orbitals and a distorted atomic configuration that we assign to a pseudo Jahn-Teller effect [9]. Negatively charged V dopants and dopant pairs in WSe_2 exhibit a series of occupied p-type defect states above the valence band edge, accompanied by an intriguing electronic fine-structure that we attribute to many-body electron interactions [10].

The vast chemical versatility of 2D TMDs combined with the atomic-scale characterization by scanning probe microscopy, offers a unique access to probe fundamental physical interactions at low dimensions.

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Scanning tunneling spectroscopy of van der Waals bilayers - from moire superlattices to moire quasicrystals

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The emergence of moiré superlattice (MSL) designed using van der Waals materials (vdW) bilayers has created unprecedented opportunities to engineer 2D electronic materials with novel properties. Thus far, most superlattices are created at small twist angles ($\theta_t \leq 6^0$). At small angles, the moire pattern is either commensurate or nearly commensurate to the atomic lattice. Moreover, the moiré wavelength is long, and regions with different interlayer alignments within the moiré unit cell can be treated individually as a local region with different electronic structures (local approximation).

At a large twist angle, the moiré patterns are in general incommensurate with atomic lattices except for a few rare exceptions. One well-known commensurate structure at a large twist angle of $\theta_t = 21.8^0$, is a root 7 by root 7 structure whose lattice constant is rather small (< 1 nm). Here we adapt the terminology "moire crystal" to make a distinction from the more superlattices. At $\theta_t = 30^0$, an incommensurate moire structure is formed that breaks the translational symmetry but possesses a dodecagonal rotational symmetry. While the translational symmetry is broken, long-range order exists, yielding sharp diffraction patterns without translation symmetry. By using scanning tunneling spectroscopy, we will uncover the electronic structures in these three regimes: moire superlattices, moire crystals, and moire quasicrystals. As the Bloch theorem is not applicable, understanding the electronic structures of moire quasicrystals is particularly challenging. I will show how valley-resolved scanning tunneling spectroscopy allows us to uncover how the interlay Umklapp scattering of different orders manifest the formation of a dense set of mini gaps.

Electron microscopy and spectroscopy of 2D hybrid materials

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Electron microscopy and spectroscopy are widely used to characterize various low-dimensional materials. Identifying the atomic structures and/or measurements of local optical properties are of great importance in designing nanoscale devices based on hybrid nanostructures. Electron energy-loss spectroscopy (EELS) has been used for elemental identification in transmission electron microscopes (TEM) by using core-level excitations. Recent developments of monochromators after the e-beam guns have enabled us to access optical and vibrational information from the valence EELS ranges of nanometric materials. Here we show our latest studies to develop the possibilities of EELS applied for low-dimensional hybrid materials. Examples for atomic defects in in-plane hybrid TMDCs[1], monolayer structures of metal chlorides intercalated in bi-layer graphene[2, 3], surface adatoms for catalysis[4], isotopically heterogeneous graphene[5], and some forms of novel low-D structures[6] will be shown.

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Atomic scale mapping of the electric field and charge density in BN nanostructures by 4D-STEM

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Electric field variations at the atomic scale are crucial in determining the physical and chemical properties of 2D defective materials, such as reactivity, interface effects, and molecule rearrangement. However, imaging these changes at an individual atom sensitivity and space resolution is a significant challenge.

Recently, 4D-STEM imaging has emerged as a promising technique to achieve this goal. In 4D-STEM experiments, a 2D convergent beam electron diffraction pattern is acquired at each probe position, generating a 4D dataset. The displacements of the center of mass (COM) of the diffraction pattern are directly related to the interaction between the electron beam and the electrostatic field during its propagation through the material [1-3]. The 2D vectorial map of the electric field can then be obtained with atomic resolution from which the charge density distribution can be extracted. While probe propagation cannot be neglected in thick samples, the technique is in principle quantitative for weak phase objects [4].

In this work, we present 4D-STEM analysis performed on perfect and defective mono- to few-layers h-BN flakes. We compare these experimental results with field image simulations obtained by propagating the electron probe within the Coulomb potential extracted from full-potential density functional theory calculations. Our results demonstrate that the method is fully quantitative when both electronic and nuclei charges are considered. We show how this technique is particularly effective in the localization and structural determination of defects beyond the conventional imaging techniques.

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How ab initio calculations can help identifying useful defects for quantum technology

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I will briefly introduce the Computational 2D Materials Database (C2DB) as an open digital platform for 2D materials research [1,2]. Next, I will present a recent first-principles based screening for optically accessible, high-spin point defects in wide band gap 2D crystals. Starting from an initial set of more than 10k point defects, comprising both intrinsic and extrinsic, single and double defects in ten 2D host materials, we identify 610 defects with a triplet ground state. For these defects, we calculate the hyperfine coupling and zero-field splitting tensors. For the subset of these triplets exhibiting the lowest Huang-Rhys factors, we calculate the full photo-luminescence (PL) spectrum. Our approach reveals many new spin defects with narrow PL line shapes and emission frequencies covering a broad spectral range. Most of the defects are hosted in hexagonal BN, but some are also found in other hosts. All the data will be made available in the open access QPOD database [3]. If time allows, I will discuss a joint theory-experimental study employing photo luminescence excitation (PLE) spectroscopy to explore the excitation mechanism in carbon-based point defects in hBN [4].

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Influence of intrinsic and extrinsic defects on the electronic and photonic properties of TMD monolayers

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Abbe Center of Photonics (ACP)

Presence of the intrinsic and extrinsic defects in two-dimensional (2D) materials has crucial influence on their physical and chemical properties, observation of fundamental phenomena and performance in devices. In this contribution, I will present our investigation of the defect role in transition metal dichalcogenides (TMDs) monolayers (MLs) and their heterostructures based on several case studies. (i) Rise of the giant persistent photoconductivity due the point defects in TMD MLs [1]. (ii) Influence of the h-BN encapsulation on the optical performance of TMD MLs grown by chemical vapor deposition (CVD) [2]. (iii) Influence of the substrate passivation on a significant increase in the performance of TMD ML based devices. (iv) Influence of a low defect density on the photoluminescence (PL) linewidth and observation of the Zeeman splitting in Janus SeMoS MLs [4]. (v) Influence of the grain boundary width in lateral $MoSe_2$-WSe_2 heterostructures on the exciton diffusion [5].

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Extended defect production in 2D materials by the impact of individual slow highly charged ions

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Slow heavy ions trigger material damage at solid surfaces typically by momentum transfer and the subsequent formation of a collisional cascade between recoils in the material. In freestanding 2D materials an extended collisional cascade cannot evolve and as such individual ions can produce only single defects or small defect clusters by direct knock-on damage. However, utilizing the fact that ions can be prepared in different charge states and that these charge states are linked to a high potential energy stored within the ion itself, one can trigger electronic damage in a single monolayer of material [1].
In state-of-the-art sources for highly charged ions, heavy species like Xe can be ionized to a high degree and in our particular experimental setup we are able to produce up to Xe^{44+} ions storing about 40keV potential energy with an adjustable kinetic energy ranging from about 40keV to 400keV.

The impact of a slow highly charged ion on a 2D material leads to the transfer of the potential energy to the surface and subsequent excitation of charge carriers on a nanometric area. Depending on the response of the material to this large perturbation of the electronic subsystem, energy dissipation in the layer may occur (in case of metals) or localized electronic excitations may couple to lattice atomic motion (in case of low-mobility materials). Consequently, extended damage may be observed as pores on the nanoscale in, e.g., freestanding MoS_2 monolayers [2]. In freestanding van-der-Waals heterostructures produced from MoS_2 and graphene only the MoS_2 layer can be perforated and only if the layer faces the incoming ion beam [3].

In this contribution I will discuss the mechanism of electronic sputtering by slow highly charged ions and present recent results on nanopore formation highlighting the unique features of this damage mechanism to address only a single surface layer in a stack van-der-Waals-coupled layers.

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Graphene nanoribbon junctions as elementary components of nanoelectronic circuits

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On-surface chemical self-assembly of graphene nanoribbons (GNRs) has opened the possibilities for producing complex graphene-based nanostructures with atomic precision [1]. Two- and multiterminal junctions in GNRs – essentially defects in these one-dimensional nanostructures – can be considered as elementary components of complex all-graphene nanoelectronic circuits [2]. We aim at establishing the design principles of such graphene-based nanoelectronic circuits by revealing the relations between the structure of GNRs junction and their electronic transport properties. The work is performed by means of first-principles and model Hamiltonian calculations combined with exhaustive high-throughput screening. We first focus on two-terminal GNR junctions with linear configurations being the simplest examples for which a sufficient body of experimental results is available (e.g. Refs. 3-7). Angled GNR junctions are more complex and are inevitable in the interconnects of nanoelectronic circuits. We systematically address the electronic transport properties of 60 and 120 degrees angled GNR junctions exploring ca. 400,000 distinct configurations, which allows us to formulate general guidelines into the engineering of transport properties of GNR circuits and identify a large number of junctions that have conductance close to the limit defined by the ballistic conductance of ideal GNR leads [8]. A user-friendly online application for modeling and calculation of the electronic transport properties of GNR junctions is presented [9].

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First-principles analysis of the point-defects influence on spectroscopic properties of CdSe nanoplatelets

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CdSe colloidal nanoparticles are a material known for their spectroscopic properties as well as the tunability of their optical properties. It is why they are efficient materials for producing optoelectronic sensors and LEDs. Recently novel studies have found out, that in the metal-doped CdSe nanoparticles, the emission originating from the relaxation of the defect can cover the excitonic emission [1]. Thus, it is essential to theoretically investigate the defect formation energies of the copper and silver to find out which sites of the impurities are the most accessible and to examine the defect recombination pathways in CdSe. In this study, copper and silver were doped into 3-5 monolayer-thick CdSe nanoplatelets via cation exchange synthesis [2]. Single particle spectroscopy of the nanocrystals reveals the red shift of the emission, which is directly correlated to the transition levels of the point defects. The results provide insight to the stimulated excitonic emission mechanism.

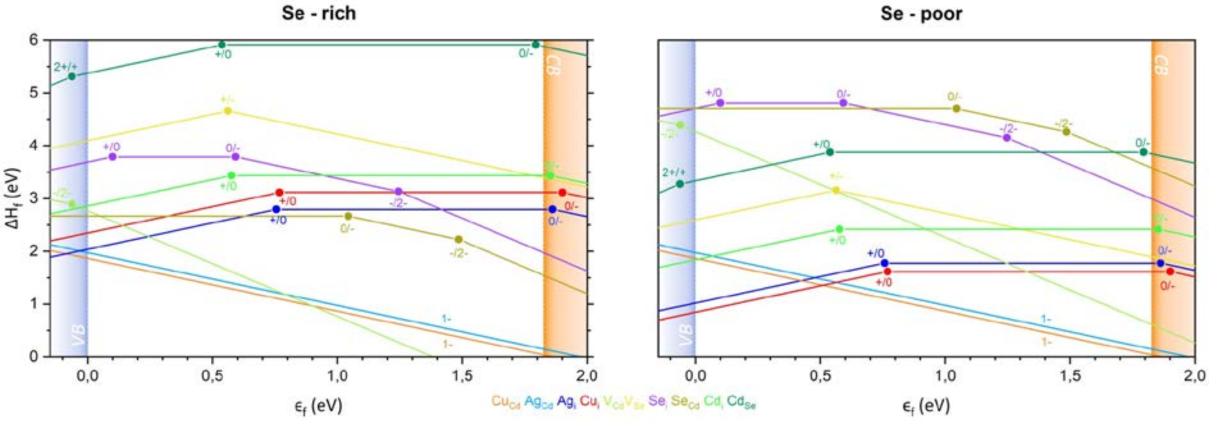

Fig. 1. Defect formation energies as a function of Fermi energy for selected impurities at Se-poor and Se-rich conditions, respectively.

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Abstracts of Posters

(in alphabetical order)

Atomistically-informed phase-field fracture modeling of defective graphenes

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In this study, we develop an atomistically-informed nonlocal phase-field formulation based on Griffith's theory of fracture to investigate crack propagation in defective graphenes. For this, molecular dynamics (MD) simulations are performed to obtain material parameters, including Young's modulus, Poisson ratio, the critical energy release rate, and the small-scale parameter. The properties are then used in phase-field continuum simulations to define the Helmholtz free energy. A tension/compression split of the free energy is considered to prevent cracking in regions under compression. Furthermore, the continuum model's capability to predict the fracture behavior of defective graphenes is evaluated using MD simulation results. Finally, it is shown that the combination of MD and phase-field simulations is a well-founded approach to identifying the defect-dependent response of graphenes.

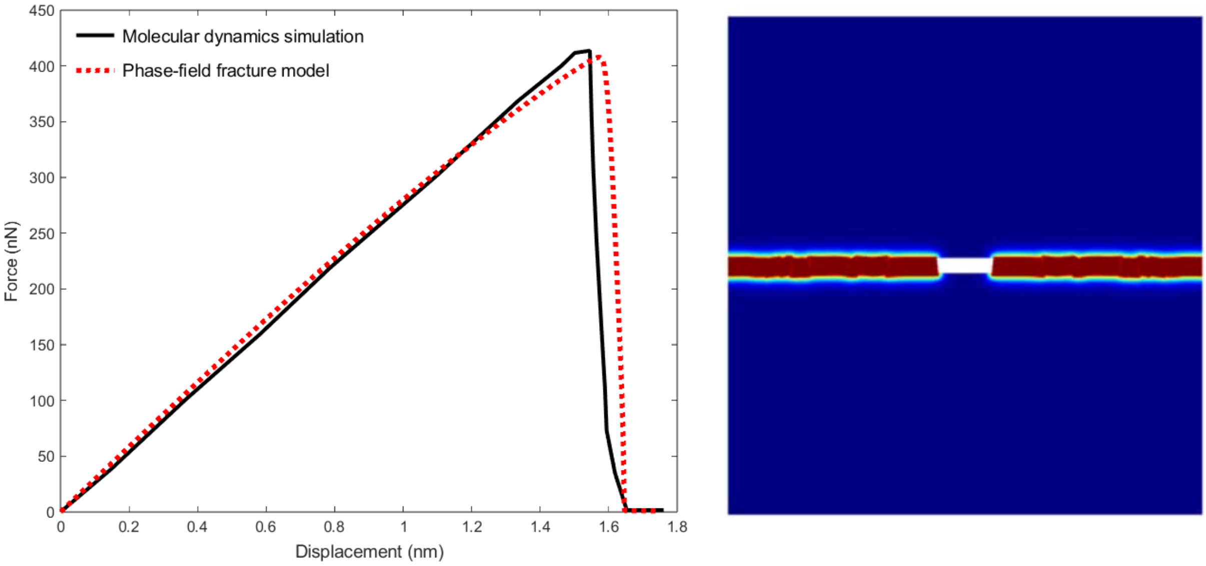

Figure 1. Fracture behavior of a 55x55 nm^2 graphene under unidirectional tension: (a) force-displacement response, and (b) fracture pattern.

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A density functional theory investigation into the origin of p-type doping in MoS_2 via Ultraviolet-Ozone Treatment

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Molybdenum disulfide (MoS_2), one of the van der Waals transition metal dichalcogenide semiconductors, has attracted great interest in recent years in the field of optoelectronics due to its 2D nature and potential for applications in many devices. Applications such as all-MoS_2 transistors require p- and n- type MoS_2 to be reliably produced without dramatically changing other properties of the material such as the band gap energy. Such devices are highly attractive due to their 2D nature providing a route to increasing the number density of such devices. They can also be fabricated on a great variety of substrates, including wearables [1]. As-grown MoS_2 is an n-type semiconductor; one method of achieving a transition to p- type MoS_2 is via surface treatment using UV-ozone, which we have experimentally achieved in mono- to few- layer systems. To further understand through which mechanism this transition occurs, we undertake DFT calculations using a mixture of both PBE and hybrid levels of theory to assess which possible oxygen species have the potential to trap charge. This is achieved by explicitly adding charge to the various possible defects to visualise if the added electron localises at the defect site, as well as assessing the thermodynamic stability of such defects. Our work has identified some candidate defects with the potential to localise charge have been identified, namely atomic and diatomic oxygen adsorption. With this understanding, we provide an easy route to engineer the optoelectrical properties of these 2D layered materials for devices such as transistors, LEDs and lasers [2,3].

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An Ultrafast STM Probing the Dynamics at Single Defects in 2D Materials

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Point defects in 2D transition metal dichalcogenides (TMDs) are perfect model systems to investigate strongly correlated dynamics in low dimensions [1]. This requires ultrafast time & atomic spatial resolution that can typically not be achieved simultaneously. Here, we develop a tool, which combines ultrafast pump-probe THz spectroscopy with scanning tunneling microscopy (STM) [2]. The specialty of our system is the highly efficient generation of phase-stable single-cycle THz pulses at variable repetition rates up to 40 MHz, while being able to continuously tune the carrier-envelope phase of the pulses [1]. The tailored THz pulses are focused in the STM junction by a high numeric aperture parabolic mirror. By precisely characterizing the THz near- and far-field waveform and its amplitude, state-selective tunneling into specific defect states with sub ps-temporal control becomes possible. Thereby we extend the capabilities of conventional STMs by increasing the time resolution by orders of magnitude. The THz-STM opens a new frontier for studying defects in TMDs and other 2D materials at their native time and length-scales

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Optical properties of monolayer $MoSe_2$ implanted with ultra-low energy Cr ions

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Transition metal dichalcogenide (TMD) monolayers (MLs) exhibit a unique combination of properties that include direct bandgap in visible to near infrared range, strong spin-orbit coupling and light-matter interaction etc. which make these materials interesting both for fundamental research and potential applications in e.g. optoelectronics and spintronics. Analogously to the bulk semiconductors, manipulation of the electronic properties of these materials is of great importance for the realization of their full potential. Ion implantation has been a common technique to tune the properties of bulk semiconductors via doping. Ion implantation is a chemically clean method of doping semiconductors with a wide selection of elements, even those thermodynamically unfavorable. It is also promising for doping of 2D materials but requires low ion energy to be effective and to maintain the materials' lattice integrity. This work explores the optical properties of $MoSe_2$ ML implanted with Cr ions at the energy of 25 eV and fluence of $3x10^{12}$ cm^{-2}. A Cr-related photoluminescence signal was observed under a weak n-doping. This signal showed low saturation threshold, characteristic of low defect densities, at laser excitation intensity of about 5 μW/μm^2. The lifetime of several nanoseconds is much longer than that of the excitonic emissions, while its magnetic response is weaker (g-factor ≈ -1). Ab-initio simulations of the implantation process and band structure calculations of the $MoSe_2$ ML containing Cr atoms aid the identification of defect configurations, which could be responsible for the observed behavior. Those include Se adatom bound to a Cr at Se site, and a Cr substituting a Mo atom. This work demonstrates that molecular dynamic simulations of the implantation process combined with the DFT calculations of the implantation products' band structure are a very powerful tool to understand and guide the functionalization of 2D materials using low-energy ions.

Creation of single vacancies in hBN with electron irradiation

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Two-dimensional (2D) materials including graphene, hBN, and TMDs have been extensively studied due to their exceptional properties. However, defects in 2D materials are ubiquitous, which could have detrimental or beneficial effects by altering their intrinsic properties.

Aberration-corrected scanning transmission electron microscopy (STEM) imaging has been routinely used to investigate their atomic structure and chemical nature. However, materials can also damage due to the interaction with the energetic electron beam. Analyzing the damage rate gives information about the stability of the material under irradiation, establishing safe limits for their reliable characterization.

Irradiation effects are well understood in the case of metallic graphene, where pure elastic knock-on damage provides a good quantitative description [1]. For semiconducting MoS_2, a combination of elastic and inelastic effects appears to be active [2]. For insulating hBN, the damage mechanism is not clear and systematic studies with controlled microscope column conditions are lacking. In earlier studies, only a pure knock-on effect was considered in the theoretical calculations [3].

We performed controlled experiments on suspended monolayer hBN using STEM in UHV at beam energies between 50 and 90 keV and measured the displacement cross sections [4]. The damage rates below 80 keV are lower than previously measured under comparatively poorer residual vacuum conditions where chemical etching is the dominant damage mechanism. We develop a theoretical description that accounts for a lowering of the displacement threshold energy due to valence ionization resulting from the inelastic scattering of probe electrons, and model using charge-constrained DFT molecular dynamics.

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Microstructural characterization of highly-disordered nanocrystalline Transition-Metal Chalcogenides prepared by mechanochemical synthesis

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The combination of several experimental techniques (XRPD, TEM, DSC, Raman) and the microstructural modeling including the volume-weighted diameter size, surface-weighted ’true’ crystallite size for an ellipsoidal domain shape as well as the Debye Function (DFA) and Pair Distribution Function (PDF) Analysis [1, 2] overcome conventional methods of analysis (notably the Rietveld method [3]) that fail to consider important information contained in diffuse scattering, typically of disordered and/or nanometric materials. Here we present some results on these modeling for the $Fe_{56}Te_{44}$ and Co_xTe_{100-x} (with x = 32, 34 and 40) samples prepared by mechanochemical route. A thorough structural and microstructural characterization of Fe_5Te_4 NPs [4], presenting an innovative microstructural model, integrating the effects of microstrain within the DFA modeling of a population of spherical NPs of variable size, indicates the presence of highly strained nanoparticles, with strain accumulated in the *ab*-plane of the tetragonal structure. For γ-$CoTe_2$ nanocrystals found in Co_xTe_{100-x} (with x = 32 and 34) samples, the effective sizes considering the volume-weighted diameter and the surface-weighted ’true’ crystallite size for an ellipsoidal domain shape were about 25 nm and 13 nm, respectively [6]. Exploring both initial stoichiometries of Co_xTe_{100-x} (with x = 32 and 40), all four different phases of Co-Te system had proven possible to be synthesized via mechanochemistry [7]. XRPD results inferred that a phase transition from the most stable $CoTe_2$ Pnnm to the $CoTe_2$ P-3m1 structure within 12 h of milling for the $Co_{32}Te_{68}$ sample and, for the $Co_{40}Te_{60}$ sample, the three $CoTe_2$ polymorphs were observed from 6 h to 15 h of milling with crystallite sizes ranged from ~8 to ~20 nm with volume normalized diameter average and ~2 to ~9 nm of surface-based true crystallite size. The milling procedure inflicted strain in the crystallites that ranged from ~0.4 to ~1.5% in some Co_xTe_{100-x} samples.

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Ion induced defects in two-dimensional tungsten diselenide boron nitride heterostructure

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Monolayer transition metal dichalcogenides (TMDCs) like tungsten diselenide (WSe_2) are highly interesting materials for optoelectronic and valleytronic applications. We used Xe^{q+} ions with E_{kin}=180 keV to deliberately introduce defects into the WSe_2 lattice and compared its optoelectronic properties before and after irradiation with photoluminescence spectroscopy. Encapsulation in hexagonal boron nitride (hBN) isolates the WSe_2 from environmental influences like adsorbates and detrimental interactions with the widely used Si/SiO_2 substrates. We find differences in the photoluminescence response for encapsulated and non-encapsulated WSe_2, which can be explained by the encapsulation preventing saturation of the created vacancies by adsorbates. In particular, there are various localized excitonic states in our different sample systems, and we explain this observation with differing ion interactions with encapsulated and non-encapsulated WSe_2. Furthermore, we observe overall highly increased exciton lifetimes after the irradiation, likely caused by the longer lifetime of the localized excitons.

Interface Defect Engineering and Morphological Control of Lateral 2d Heterostructures

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The material interface is possibly the most important part of any electronic or optoelectronic device and plays a major role in heterostructure devices. However, understanding the role of defects at the interface is crucial. Our work [1] investigates defect driven material engineering of 2D lateral interfaces. Specifically, we employ first-principles modelling to examine the successfully grown interface between 2D TaS2 and MoS2, materials with incommensurate primitive cells.

We show that the interface can have two distinct morphologies, "dislocation" or "coherent", and our investigations identify competing physical features that drive the system towards either one. The system is in a balance between the local bond symmetry and material strain. Dislocations give rise to a breakdown of local symmetry and have an energetic cost for their formation; however, preventing dislocations incurs a cost in strain energy. Using these new insights, we apply these techniques to a variety of other 2D interfaces that share structural symmetry and predict their interface transition point from "coherent" to "dislocation". This is a powerful methodology applicable to any 2D material pair that share structural symmetry, and the qualitative understanding is of great value to any experimental or theoretical study. Overall, our insights provide a guideline for controlling the morphology of the lateral interfaces between 2D materials, which should be of high importance for controlling device functionalities.

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Charge-dependent symmetry breaking in Rhenium-doped MoS_2

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Atomically thin 2D materials have attracted large interest for fundamental research and are considered a key building block of next generation nanoelectronic devices. The electronic and optical properties of 2D materials are strongly influenced by defects due to the atomic confinement and reduced screening. However, the precise functionality of defects is linked to their interaction with the host lattice. Here we present the investigation of substitutional rhenium dopants in mono- and bilayer MoS_2 using scanning tunneling microscopy and CO-tip non-contact atomic force microscopy. We directly observed spontaneous symmetry breaking of rhenium dopants (Re_{Mo}) and negatively charged sulfur vacancies (Vac_S^-) due to the (Pseudo-) Jahn-Teller Effect. While Vac_S^- occur in both the symmetric and the symmetry-broken state, Re_{Mo} exhibit charge-dependent symmetry-breaking. Three different charge states of Re_{Mo} are stabilized by chemical gating induced by the difference in substrate workfunction. Intriguingly, we find larger domains of Re_{Mo} with a strong directional preference in the direction of the distortion. Through annealing we were also able to create and explore the dopant-vacancy complex $(Re_{Mo} + Vac_S)^-$ which exhibits discrete states deep inside the band gap, in agreement with DFT calculations. It is predicted to be similar to the NV^- center. By atomically-resolved mapping of electronic orbitals and geometric structures, we can identify various defects in MoS_2 and disentangle effects of spatial averaging, charge multistability, configurational dynamics, and external perturbations that often mask the presence of local symmetry breaking.

Electron Beam Induced Chemical Etching of 2D Materials in a Transmission Electron Microscope

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Transmission electron microscopes (TEM) are used for imaging 2D materials with a resolution of single atom. During characterization, the imaged material can be damaged (modified) by the beam, which gives rise to the question of the origin of the observed defects. Hence, the knowledge of the electron beam damage mechanisms is important for proper imaging. Different mechanisms such as knock-on, ionization (excitation) damage, and chemical etching have been identified [1].

In this study, the knock-on threshold energies for displacing atoms from monolayer of h-BN, graphene and MoS_2 in the presence of adsorbed adatoms (H, C, N, O) on the surface are calculated in the framework of spin-polarized density functional theory. We found that when an adatom is present on the surface, the displacement threshold energies are reduced by few electron-volts (0.5-3 eV) in some cases as compared to pristine systems. Further, we considered the additional effect of electronic excitation on the displacement threshold energies in h-BN as shown earlier for MoS_2 [2]. The displacement cross-sections under the electron beam are assessed employing the McKinley-Feshbach formalism allowing to compare different channels of damage creation.

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Local creation of point defects in two-dimensional MoS_2

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Point defects such as vacancies in semiconducting two-dimensional (2D) transition metal dichalcogenides (TMDCs) are studied in great detail because of their unique quantum properties as well as their potential for applications, e.g. as dopants [1] or single photon emitters [2]. The quantum nature of these defects originates from deep in-gap states [3] which are largely unscreened due to reduced dimensionality of the host material. Vacancies are commonly created via ion bombardment or annealing in previously pristine TMDCs, creating an ensemble of defects without atomic-scale control of their position.

Here we describe how the tip of a scanning tunneling microscope can be used to create single point defects at well-defined positions in monolayer MoS_2 on Graphene/Ir(111). Our method involves single Fe atoms, which are deposited on the surface of MoS_2 at low temperatures. Approaching the STM tip towards these single Fe atoms creates two types of defects, which are interpreted as sulphur vacancies in the top sulphur layer of MoS_2 and Fe substitutions of sulphur. The ability to laterally manipulate Fe atoms before controlled defect creation enables us to design novel artificial states, such as vacancy dimers which form molecule-like bonding and anti-bonding states.

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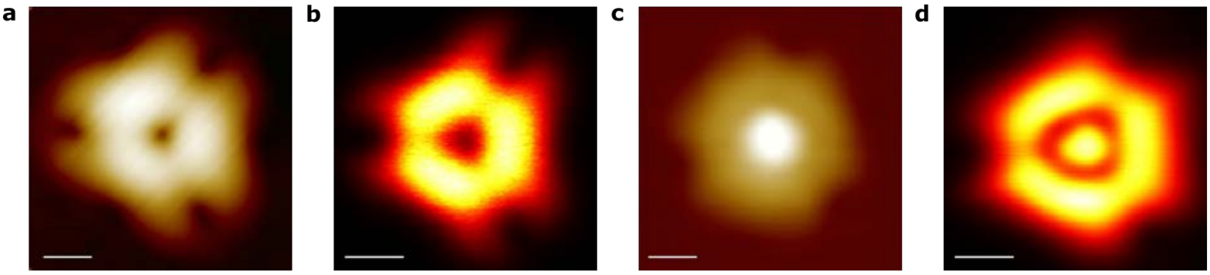

a STM topography of sulphur vacancy (V_{bias} = 200 mV, I = 300 pA) and **b** corresponding dI/dV map at 365 meV. **c** STM topography of Fe substituted sulphur vacancy (V_{bias} = 1 V, I = 100 pA). **d** dI/dV map of Fe substituted sulphur vacancy at 400 meV. The scale bars correspond to 5 Å lateral size.

Correlated AFM/STEM study on the Mechanical Stiffness of Defect-Engineered Graphene

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The first isolation of a single layer graphene sheet from graphite via the adhesive tape method in 2004 [1] triggered an avalanche of experiments studying this two-dimensional (2D) material, including investigations on the unique electronic as well as mechanical properties. Since these macroscopically observed properties are a result of elemental composition and atomic structure, the 2D nature of graphene allows for a direct correlation by linking atomic resolution scanning transmission electron microscopy (STEM) images to the observed macroscopic properties. Moreover, this structure-to-property correlation permits investigations on alterations of material properties through defect-engineering. In this study, the in-plane mechanical stiffness of graphene in its pristine state is compared to a defective state in the form of vacancies by correlating atomic force microscopy (AFM) nano-indentation measurements to atomic resolution STEM images. Both instruments, as well as the target chamber where the vacancies are created, are part of the Controlled Alteration of Nano-materials in Vacuum down to the Atomic Scale (CANVAS) system at the University of Vienna, which provides an ultra-high vacuum environment permitting direct correlation [4]. The vacancy density is precisely determined by STEM scan maps, which combine individual small field of view atomic resolution images into one large area, followed by processing of the data set by a convolutional neural network [2]. With a vacancy density of around 1×10^{13} cm^{-2} the 2D elastic modulus decreases by approximately 40%. The STEM images reveal strain-induced surface corrugation caused by the vacancies [3], which might play a role in the weakening mechanism.

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Niobium Doping-Induced Ambipolar Transport in Molybdenum Disulfide for Optoelectronic Devices

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Atomically thin molybdenum disulfide is a two-dimensional material with excellent electronic properties, thermal stability, and mechanical durability, making it an important disruptive technology in the field of optoelectronics. However, its strong n-type conductivity has impeded its development and use in p-n junction structures. To overcome this limitation, substitutional doping can be used to controllably p-dope MoS_2. In this study, direct growth of niobium-doped monolayer MoS_2 was carried out, and the doping effect was investigated using Raman and photoluminescence spectroscopy. The annealing of a niobium-doped MoS_2 field-effect transistor led to the activation of doping sites, resulting in ambipolar transport behavior instead of the previous n-type behavior. Additionally, the sulfur annealing remedied the role of intrinsic defects, as evidenced by the narrow hysteresis observed after annealing compared to the wide hysteresis seen before. These findings indicate that substitutional doping can potentially solve the problem of strong n-type conductivity in MoS_2 and pave the way for the development of the next generation of optoelectronic devices.

Competing Processes as Quality Limitation: New Insights into Microscopic Growth Mechanism of Hexagonal Boron Nitride on Ir(111)

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Despite the tremendous research efforts targeting industrial growth of two-dimensional hexagonal boron nitride (hBN), especially on transition metal surfaces, until today no growth recipe was developed, promising large domain sizes, homogeneous lattice constants and a matching orientation of layer and substrate. We studied CVD grown hBN on Ir(111) with borazine as precursor and found two competing processes governing the quality of the hBN layer on a microscopic scale: kinetic limitations after catalytic borazine decomposition and dissociation of B3N3 rings with loss of nitrogen followed by disintegration of the grown layer. The counteracting interplay of all processes sets a fundamental limit to the achievable quality, due to defect-creation upon dissociation of the rings. We combined results from spot profile analyzing low energy electron diffraction (SPA-LEED), allowing us to determine the distribution of domain orientations from a representative surface area, and low energy electron microscopy (LEEM), for the measure of domain density [1]. Our understanding of the microscopic processes during hBN growth further enable us to selectively tune the growing material, hBN or 2D Boron (Borophene), representing a potential pathway to lateral heterostructures.

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Fabrication and Polarization Dynamics Single Photon Emitters in Hexagonal Boron Nitride

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Quantum emitters in solid-state crystals have gained attention with the recent advancement of quantum technologies. In particular, color centers in hexagonal Boron Nitride (hBN) stand out due to their optical and physical properties featuring room temperature operation and high luminosity. The atomic structure of these fluorescent defects in hBN is still not well understood yet. Here we present the fabrication of single photon emitters in hBN using a standard scanning electron microscope (SEM), emitting at 575 nm. This fabrication process produces emitters with identical spectral and emission properties. To address the structural features of emitters, we polarization-resolve the orientation of excitation and emission dipoles in the host crystal. We find excitation and emission dipole are correlating with the crystallographic axis as confirmed with second-harmonic generation. Furthermore, density functional theory calculations are used to predict the characteristic transition dipole moments of a large number of potential defects. We have also investigated the temporal polarization dynamics and discovered a mechanism of time-dependent polarization visibility and dipole orientation. Interestingly, we also observe this in other solid-state quantum emitter systems and propose a potential explanation for this effect. We, therefore, provide a promising pathway for the identification of color centers in solid-state crystals in general, as well as important insight into the dynamics of solid-state quantum emitters.

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The role of the defects in 1D/2D charge transfer thin films of the perovskite solar cells

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Perovskite solar cells (PSCs) are classified as emerging next-generation thin-film solar cells and they receive considerable attention because of their high efficiency, low cost, low recombination rate, tuneable band gap, high mobility of charge carriers, etc. The problem that hinders their wider and more commercial application is susceptibility to both moisture and oxygen degradation, which limits their long-term stability. Among many attempts to upgrade to prevent the early degradation of the PSCs, finding the optimal PSC configuration arose as a viable tool. Configuration wise, various charge layer (CTL) interfaces were investigated, focusing on the nanostructured CTLs.

Here, we aged the PSCs at ambient conditions or at elevated temperatures; an in-situ setup was established comprising synchrotron grazing incidence diffraction and Raman spectroscopy as a function of temperature under ambient and isothermal conditions. Measurements of current-voltage characteristics and electron microscopic investigations were conducted separately. We investigated PSCs in n-i-p configuration comprising a rubidium-caesium-methylammonium-formamidinium lead iodide/bromide perovskite absorber, interfaced with nanostructured ZnO-nanorod or mesostructured TiO_2 CTL.

Broad characterisation suggested different degradation rates exist for different CTLs. Scanning transmission electron microscopy of lamellas, derived by dual beam microscopy, revealed that the origin of the degradation lay in the CTL/absorber interface. For the case of the nanostructured zincite, the perovskite absorber contained many defects, leading to the conclusion that the investigated quadruple perovskite absorber showed limited compatibility with ZnO nanorod CTL. Morphological defects nullified the advantages initially achieved by nanostructuring. The exchange of the ZnO nanorod CTL with mesostructured TiO_2 improved the stability parameters of the absorber layer.

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Oxygen-mediated defect formation and degradation in 2D MoS_2 and $MoTe_2$

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Interactions of two-dimensional materials with environmental gases often result in alteration of their properties and degradation. Understanding chemical reactions in these materials under ambient conditions is therefore of critical importance for their practical applications. To understand the effects of oxygen on defect formation and degradation in transition metal dichalcogenides (TMDs) we have studied single layers of MoS_2 and $MoTe_2$ in situ in an electron microscope under low-pressure ($9 \times 10^{-10} - 4 \times 10^{-7}$ torr) oxygen environments. It is found that defects formation in MoS_2 is independent on the partial oxygen pressure and is caused by the electron beam damage. In contrast, $MoTe_2$ is highly sensitive to the presence of oxygen and shows significant damage above the pressure of 1×10^{-7} torr. Moreover, the etching rate of $MoTe_2$ substantially increases at the areas covered by hydrocarbon contaminations.

To reveal the underlying mechanism of the oxidative etching in $MoTe_2$ we used density functional theory calculations. Our results show that adsorption of oxygen radicals on neighboring Te atoms enables an energetically favorable reaction pathway for oxygen intercalation that results in appearance of a weakly bound (0.21 eV) TeO pair on top of the surface which can easily desorb. Therefore, etching of $MoTe_2$ by oxygen radicals can occur even for a non-defective monolayer. In contrast, in MoS_2 such a process is associated with high energy barriers and is not feasible at room temperatures. Further, it is found that in $MoTe_2$ atomic carbon preferentially adopts interstitial configuration, which can significantly affect the properties of the material, as well as defect formation and oxidation mechanisms. Our results provide an important insight into the oxygen-mediated structural changes in TMDs.

Raman features of gas-phase-grown WS_2 monolayer flakes: Influence of precursor molar flow rate on quality

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Gas-phase chemical vapor deposition (CVD) is the preferred method of fabrication for 2D transition metal dichalcogenides (TMDs) with excellent optoelectronic properties. The CVD growth parameter that most influences the quality of the resulting TMDs is the molar ratio of precursor flow rates. Typically, Raman spectroscopy is used to evaluate such films, but studies on the correlation between Raman features and molar flow rates are very scarce. Here, we investigate the influence of precursor molar flow rate on characteristic Raman modes of the WS_2 monolayer flakes. The WS_2 flakes were fabricated on c-plane sapphire using low-pressure gas-phase CVD and precursor molar ratios ranging from 470:1 to 8100:1 [H_2S/bis(tert-butylimido) bis(dimethylamido) tungsten)]. Raman spectra of the WS_2 flakes were recorded in the back-scattered geometry. A thorough analysis of the Rama mode position, area, intensity (amplitude), and FWHM were carried out using Lorentzian fitting. Quality exhibiting Raman features (intensity & FWHM) decreased as the molar ratio increased for in and out-of-plane modes. We identified 2100:1 as the optimum precursor molar ratio for obtaining high-quality flakes. In addition, for the out-of-plane mode, the FWHM revealed that at lower sulfur concentrations the as-grown flakes had quality-degrading sulfur vacancy defects. Overall, our findings contribute to the development of new growth routes for high-quality TMDs via gas-phase CVD. All the results will be presented and discussed in detail.

Structural Defects in Janus MoSSe Monolayer: A Density Functional Theory Study

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Two-dimensional layered materials with different anions on both faces of each layer, called Janus monolayers, have attracted significant interest due to their unique structural asymmetry perpendicular to the layer, which gives rise to an electric dipole moment that further diversifies the versatile properties of the transition-metal dichalcogenide materials class. However, the synthesis of a material such as MoSSe is prone to the introduction of various point defects, which could significantly modify the electric and optical properties as well as vibrational spectra. Using density functional theory, we provide an in-depth insight into the thermal stability of numerous point-vacancy and anti-site defects in the Janus MoSSe monolayer. The structural changes are discussed in terms of the local strain induced by the modified atomic bonding around the defect sites. The electronic structure and linear optical response of Janus MoSSe monolayer with various point defects are studied, and possible fingerprints of electronic transitions due to defects are rationalized. First-principles calculations of phonons are carried out to spot the fingerprint of each point defect in the vibrational spectrum of the Janus MoSSe monolayer. Our systemic study will provide a broad picture of the roles the point defects could play in modifying and tuning the electronic and optical properties of 2D Janus materials and thus help customizing them for certain applications.

A TEM preparation technique to relate the electronic signature of defects with their atomic structure

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Atomic-resolution transmission electron microscopy (TEM) is the most suitable technique for characterizing the structure of two-dimensional (2D) materials at the atomic level. Low acceleration voltages of 20-80 kV, combined with spherical and chromatic aberration correction (CC/CS-correction), allow for atomic resolution while maintaining good control over electron-beam-induced modifications in the sample [1]. However, unlike TEM experiments that are usually performed with freely suspended 2D materials on TEM grids, many other characterization techniques, such as electrical transport measurements, require the 2D materials to be placed on different substrates [2]. This presents a challenge in linking electron microscopy with complementary characterization techniques as samples may need to be transferred from TEM grids to other substrates following the TEM investigation.

In our work, we aim to engineer quantum dots (QDs) by producing controlled defects in TEM experiments for subsequent electrical transport measurements and photoluminescence experiments. These QDs are promising platforms for quantum information storage [3]. To achieve this, we exfoliate transition metal dichalcogenides (TMDs) onto polyvinyl-alcohol-coated SiO2 and then transfer them to TEM grids for defect engineering and imaging. However, we observed that the exposure to the electron beam caused the TMD flakes to adhere more strongly to the TEM grid when transferring them back to an arbitrary substrate. To address this challenge, we present a novel "reverse transfer" preparation technique that enables the transfer of electron-exposed TMD flakes from a TEM grid to arbitrary substrates. We demonstrate proof-of-principle experiments, showing that we can transfer the TMD flakes and measure the produced defects in photoluminescence and transport measurements.

In summary, our work provides a solution to the challenge of linking electron microscopy with complementary characterization techniques, by presenting a "reverse transfer" preparation technique that allows for the transfer of electron-exposed TMD flakes from TEM grids to arbitrary substrates. This technique enables the measurement of defects produced in TEM experiments using photoluminescence and transport measurements.

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One dimensional Defects in Epitaxially Grown CrS_2 Monolayer

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Molecular beam epitaxy of transition metal dichalcogenides (TMDCs) results in the formation of edges and often also grain boundaries are formed when islands grow together [1]. These edges and boundaries are line defects and their properties differ from the two-dimensional bulk of the TMDC. Heretofore, various low- and high-symmetry grain boundaries and edges have been theoretically and experimentally investigated in TMDCs [1,2]. However, thus far, line defects have never been experimentally studied in magnetic transition metal dichalcogenides, like chromium disulfide (CrS_2).

Here we have grown monolayer H-CrS_2 by molecular beam epitaxy on graphene/Ir(110) surface and investigated with low-temperature scanning tunneling microscopy. We observed various types of low- and high-symmetry grain boundaries. Interestingly, we found two unique types of high symmetry grain boundaries, namely an antisymmetric armchair boundary and a new type of mirror twin boundary. We observe that these boundaries display characteristic commensurate periodic modulation close to $\sqrt{3}a$ (AAB) and 2.5a (MTB), with $a = 3.42 \pm 0.04$ Å, representing the CrS_2 lattice. Such boundaries have been elusive in TMDCs and similar descriptions are found for artificially created boundaries in h-BN [3]. Furthermore, monolayer CrS_2 is surrounded by S-terminated zigzag edges forming a one-dimensional wire-like structure displaying a $2a$ charge modulation. We characterize the electronic structure of the different types of line defects with high-resolution scanning tunneling spectroscopy and discuss it in terms of charge density wave physics.

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Comparison of machine learning strategies in the high-throughput exploration of ABO_2 delafossites

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The advent of machine learning introduced new techniques to considerably expedite materials discovery. This raises a fundamental question about how they balance interpretability versus accuracy. We address this aspect by comparing ensemble-based active learning (AL) of neural networks (NN) [1,2] and the sure independence screening and sparsifying operator (SISSO) [2] for the prediction of formation energies, lattice parameters and stacking in the layered ABO_2 delafossite oxides. To this end, we generate a consistent dataset from first principles. Element embedding is found to be superior to scalar input strategies, e.g., atomic properties. In conjunction with AL, the NNs reach DFT accuracy, allowing for a significant acceleration of high-throughput materials screening. In contrast, the precision of the physically interpretable SISSO descriptors is limited by the high data complexity. We combine ABO_2 infinite-layer, ABO_3 perovskite [1,2] and the delafossite data to extend the unsupervised AL into the structural space, thereby enhancing the sample efficiency in the spirit of transfer learning. Finally, we compile a phase diagram that compares the relative stability of the three distinct oxide materials classes.

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Effects of tensile strain on the formaiton energy of point defcts in 2D h-BN

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Substitutional carbon impurities in hBN have been shown to be the sources of single photon emission. Using first-principles calculations we studied the energetics of various defects formed by carbon substitution at the place of boron and nitrogen atoms as well as their combination as a function of biaxial tensile strain. We found that the formation energy of defect with carbon at the place of boron increases with increasing biaxial strain and for defect with carbon at the place of boron it decreases. We further studied how the electronic structure of the system with defects depends on tensile strain. Our results indicate that strain engineering can be used to control relative concentrations of defects and tune the characteristics of single-photon emitters.

Imaging ellispometry for identification and characterziations of 2d-materials

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In the research on two-dimensional material, hexagonal boron nitride hBN is of still growing interest as inert encapsulation layer [1], ultrathin gate dielectric [2] and as host for promising quantum emitter [3]. However, the search of micromechanical exfoliated flakes with distinct number of layers as well as fast end non-destructive characterization is difficult.

Here, we utilize ellipsometric contrast micrography to localize flakes of a required thickness. An ellipsometer measures the change of polarization induced by the investigated sample. Therefore, an ellipsometer consists of a polarization state generator (PSG) and a polarization state analyzer (PSA). In an imaging setup PSG and PSA are combined with an objective and CCD-camera to obtain microscopic images of the change of polarization. If PSA and PSG are static, ellipsometric contrast micrographs (ECM) can be recorded with the CCD-camera offering high-sensitive images, that are able to display minor differences in thicknesses below nm.

Our approach to achieve the localization of a flake of desired thickness on a known substrate, is by measuring a relative contrast of flake to substrate by ECM. Another approach allows to calculate the relative contrast of flake to substrate and thus enabling the localization of flakes with specific layer numbers on unknown substrates. An optimization of measurement parameters is shown and can improve sensitivity while increasing speed of scanning time. Parameters as e.g. wavelength, rotational angles of polarizer, analyzer, compensator and angle of incidence are taken into account to optimize measurement settings. After localization, spectroscopic ellipsometric measurements from UV to NIR are taken, to investigate the dielectric response of the exfoliated 2D flakes.

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Band parameters of group III–V semiconductors in wurtzite structure

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Group III-V semiconductors form extremely important material group, crucial for semiconductors industry and solid state physics, therefore they have been intensively studied both experimentally and theoretically. Physical properties of these materials are subject of many books and scientific publications. Situation is very different when one considers other than cubic crystallographic systems, in particular wurtzite form. While most of III-V semiconductors naturally grow in the zinc blende structure, they may also form wurtzite nanowires in special growth conditions. For modeling such structures, the properties of crystals in the bulk wurtzite form are needed as a reference, but since such data are not available (except for nitrides), one has to extract these parameters from nanowires measurements which is a challenging task.

The presented work has a predictive character. We perform systematic DFT study of a wide range of materials in wurtzite crystallographic structure. Our aim is to deliver complete set of parameters, which are needed for modeling nanostructures containing wurtzite form of III-V semiconductors. The main goal is a description of the electronic band structures and their behavior under strain conditions as it is crucial from applications point of view. In order to do so we parametrize our DFT results by 6kp model. Additionally, we investigate into the structural, elastic and piezoelectric properties of studied materials. We used the VASP code and MBJ potential which allows for accurate description of band structures and at the same time it is a computationally relatively cheap. Our results are in good agreement with available experimental and other theoretical results.

The influence of the surface on the response of GaN to Strongly Ionising Radiation

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The response of Gallium Nitride (GaN) to strongly ionising radiation is essential for the development of radiation-hard semiconductor devices. Although GaN is known for its high radiation resistance, predicting the effects of ionising radiation remains a challenge due to the complex phase-transition diagrams and defect creation-annihilation dynamics associated with group-III nitrides. In this study, we employ the Two-Temperature Model, Molecular Dynamics simulations, and Transmission Electron Microscopy to investigate the interaction of Swift Heavy Ions (SHI) with GaN.

The results reveal that GaN has a high propensity to recrystallise the region melted by the impinging ion, resulting in high thresholds for permanent track formation. However, we find that the surface reduces the confinement of the molten track, which hampers the recrystallisation process and also to a considerable amount of sputtering. Ultimately, this reduces the track formation threshold and leads to the formation of shallow voids, pits and nanohills. These findings provide crucial insights into the effects of ionising radiation on GaN, highlighting the importance of considering surface effects for a comprehensive understanding of radiation damage in this material.

Understanding the role of defects in WS_2 layers in contact with ZnO

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The remarkable properties of two-dimensional (2D) materials have garnered significant attention in recent years, and understanding their fundamental behavior is critical for developing next-generation technologies. In this study, we investigate the microscopic behavior of a 2D material, WS_2, through first-principles calculations. Specifically, we aim to elucidate the role of defects in WS_2 layers at the interface with ZnO. Using density functional theory calculations, we examine the electronic structure and binding properties of the WS_2/ZnO interface, including the impact of point defects such as vacancies and substitutions. Our results demonstrate that defects can significantly modulate the electronic properties of the interface, including charge transfer, band alignment, and chemical reactivity. These insights provide crucial information for the design and optimization of devices based on 2D materials, and offer a pathway for enhancing their performance in a wide range of applications.

Single Charge Transport through Atomic Defects Embedded in 2D Materials

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Energy spectroscopy of strongly-interacting phases requires probes that minimize screening while retaining spectral resolution and local sensitivity. Such probes can be realized by integrating quantum dots, which have sharply-defined discrete energy levels, into tunneling circuitry. In the past few years, our group has developed the use of naturally occurring defects in 2D materials as atomic-sized quantum dots. These dots exhibit sharp Coulomb blockade features with charging energies higher than 100 meV.[1,2] We have used atomic defects, acting as quantum dots within tunneling devices, to measure the density of states of monolayer graphene. At high magnetic fields, the defect-dots have shown the capability to measure variations in the chemical potential alongside excited-level spectroscopy with unprecedented resolution.[1] Also, when placing defects in proximity to a van der Waals superconductor, we showed that dot-assisted transport, through the sharply defined energy level of the quantum dot, can serve as a sensitive spectrometer.[2]

A major challenge in further developing this method is the a-priori detection of individual defects. Here we report the use of conductive Atomic Force Microscopy (cAFM) to locate and characterize these defects at room temperature. Using cAFM, we map the local conductance through an exfoliated insulator such as MoS_2 or WS_2, mounted on a conducting surface. When a finite voltage is applied to the cAFM tip, the resulting current flowing between the tip and the sample ground is integrated into a current-map image, which reveals the location of atomic defects. The individual defects each exhibit a distinct onset voltage for measurable current flow, and appear as replica of the shape of the tip. In the next stage, we plan to pattern gates and electrodes around the defects, revealed this way, to address them in low-temperature transport experiments.

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Simulating False Vacuum Decays in a Two-Dimensional Mesoscopic Quantum System Using Programmable Quantum Annealing

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Emergent metastability in non-equilibrium quantum systems is a subject of interest in numerous fields ranging from biology to cosmology[1,2]. In condensed quantum matter, a good topical example is the metastability of topologically inhibited self-organization of electronic domains in a correlated electronic crystal in the aftermath of a symmetry-breaking phase transition[3]. Understanding the dynamics of such systems is crucial for developing new quantum technologies and exploring fundamental aspects of many-body non-equilibrium quantum mechanics. Here we investigate a new approach to modelling of emergent non-equilibrium quantum behavior using a noisy programmable quantum processor (P) to simulate the observed dynamics of the quantum material (M). The success of these simulations critically depends on the faithfulness of the model correspondence between the two systems and management of the decoherence pathways. Here, for P, we use an array of qubits in a noisy superconducting quantum simulator (NSQS) without error correction, with mutual qubit interconnections that correspond directly to the electronic interactions of the material. Crucially, both systems are coupled to external noise sources of decoherence with a characteristic 1/f noise spectra, which is important for P to faithfully emulate M. Using this approach, we find that the time evolution of quantum electronic domain dynamics of M in the aftermath of the transition, and its temperature dependence measured by scanning tunnelling microscopy can be simulated solely on the basis of microscopic electronic interactions. The remarkably faithful simulation demonstrates the potential of NSQSs for studying emergent non-equilibrium dynamics in complex quantum materials.

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Low-Energy Ion Irradiation with an Electron Beam Evaporator

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The control of the ion energy is crucial for the ion implantation of two-dimensional (2D) materials. It must be high enough to remove an atom from the 2D lattice on the one hand, and low enough to remain in the lattice on the other. The lower limit for the ion implantation is the threshold energy for the atomic displacement. This energy depends on the binding energy of the atoms of the 2D material and on the chemical interaction between atom and ion. Therefore, it is different for the different elements in 2D compounds such as hexagonal boron nitride or transition metal dichalcogenides. To create single-type defects in these materials, ion beams with a low energy distribution must be used[1]. Usually, the ions are extracted with ion energies of several keV and an energy distribution of several tens of eV, which corresponds to the energy distribution of the ion source. The ion energy for implantation is set via a bias voltage applied to the sample. Here, we present a simple and robust approach for the ion generation from an electron beam evaporator. This has the advantage of a relatively small ion energy distribution of 15 eV and less, and in addition numerous different metal ions can be easily extracted. An electrostatic analyzer is used to filter out the neutral atoms and to improve the energy distribution of the ion beam to below 1.5 eV. The ion energy is between 300 eV and 800 eV. Therefore, further energy reduction is required for implantation in 2D materials, which can be done by applying a bias voltage to the sample.

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