O 53: 2D Materials IV: Graphene (joint session O/TT)

Time: Wednesday 15:00–18:00 Location: MA 005

O 53.1 Wed 15:00 MA 005

Ultra-large polymer-free suspended graphene films — •Lukas Kalkhoff, Sebastian Matschy, Ann-Sophie Meyer, Leon Lasnig, Nele Junker, Lars Breuer, and Marika Schleberger — Universität Duisburg-Essen, Fakultät für Physik, Germany

The quest to preserve graphene's unique characteristics has intensified the demand for advanced preparation methods. The production of large area graphene films has been constrained by the necessity of a polymer film, like PMMA, during the transfer process, leading to unavoidable contaminations. In this talk, we show our approach to fabricate triple-layer graphene films, without the use of polymers, freely suspended across circular holes with diameters of 100-300 micrometers. This technique achieves a high yield and also ensures remarkable uniformity of the electronic properties of graphene, both across and within individual holes [1].

Using confocal Raman and THz spectroscopy we can confirm that the structural and electronic properties of these triple-layer films are akin to monolayer graphene. This discovery has significant implications, particularly in their application as ion-electron converters in time-of-flight mass spectrometry and similar fields. Remarkably, these graphene films are two orders of magnitude thinner than conventional carbon foils used in such experiments, yet they maintain robustness and a high electron yield, as proven under picosecond ion bombardment. This marks a critical step toward replacing existing carbon films or polymer-based graphene with cleaner, more precisely defined graphene films. [1] L. Kalkhoff *et al.*, 2023, arXiv:2311.08137

O 53.2 Wed 15:15 MA 005

Design of electronic structure and transport in S-doped few-layer graphene — •Armin Sahinovic[1], Paolo Fortugno[2], Nicholas Wilson[3], Hartmut Wiggers[2], and Rossitza Pentcheva[1] — [1]Department of Physics, Universität Duisburg-Essen — [2]Institute for Energy and Materials Processes - Reactive Fluids, Universität Duisburg-Essen — [3]Department of Chemical Engineering, University of Waterloo

While the properties of N- and S-doped graphene have been addressed previously [1], the interplay between defects, doping and the layered structure of FLG are largely unknown. Based on density functional theory calculations we explore the formation energies and electronic structure of different defect types as a function of concentration and distribution. We find a layer dependence of the doping allowing for a design of the electronic structure. The surface layers are favored for doping, giving rise to buckling and a modified band structure such as a band gap opening not found for doping the center layers. Experiments on the synthesis of S-doped FLG in a microwave plasma reactor show S incorporation and a conductivity increase of up to 50%. This is consistent with the transport properties, obtained via BoltZtrap2 [2], revealing that S doping enhances the conductivity in FLG. We hereby show that tailoring the S incorporation into FLG enables one to design the electronic structure in view of energy conversion and storage applications.

[1] J.H Lee et al., Nanomaterials, 9, 268 (2019)

[2] G.K.H. Madsen et al., Comput. Phys. Commun., 231, 140 (2018)

Topical Talk O 53.3 Wed 15:30 MA 005

Tuning quantum electronic transport in nanoporous graphene — •Aran Garcia-Lekue — Donostia International Physics Center (DIPC), San Sebastian, Spain — Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Recent experimental advances have demonstrated that graphene nanoribbons (GNRs) can be laterally coupled with atomic precision to obtain a nanoporous graphene (NPG) structure with highly anisotropic electronic properties.[1] Moreover, simulations have shown that the lateral coupling of GNRs leads to sizable interribbon transmission giving rise to intriguing interference patterns,[2] and that such interribbon transmission can be switched on/off by the chemical modification of the coupling bridges.[3]

Using density functional theory (DFT) and a multiscale transport method based on DFT combined with nonequilibrium Green's functions (NEGF), we have carried out electronic structure and current simulations for different NPG systems. First, in collaboration with our experimental colleagues, we have explored a new NPG that, provided by specifically designed coupling bridges, shows additional degrees of freedom to control the in-plane current.[4] Besides, we have investigated a bilayer composed of NPG and graphene, concluding that the interlayer current can be tuned by changing their relative twist angle.

[1] Moreno et al., Science 360, 199 (2018) [2] Calogero et al., ; Nano Lett. 19, 576 (2019) [3] Calogero et al., JACS 141, 13081 (2019) [4] Moreno et al., JACS 145, 8988 (2023)

O 53.4 Wed 16:00 MA 005

Visualizing band hybridization and moiré effects in gate-tunable twisted graphene layers using nanoARPES — •Zhihao Jiang[1], Kimberly Hsieh[1], Paulina Majchrzak[1], Alfred Jones[1], Chakradhar Sahoo[1], Youngju Park[2], Dongkyu Lee[2], Kenji Watanabe[3], Takashi Taniguchi[3], Jill Miwa[1], Jeil Jung[2], Yong P. Chen[1], and Søren Ulstrup[1] — [1]Aarhus University, Denmark — [2]University of Seoul, Korea — [3]National Institute for Materials Science, Japan

Twisted graphene layers have emerged as an intriguing class of quantum materials that display surprising correlation effects, including superconductivity, Mott insulators as well as strange metal phases. The possibility to tune these states using twist angle and electrostatic doping provides a promising route to interrogate the underpinning interactions between the electronic states. Here, we use angle-resolved photoemission spectroscopy with spatial resolution at the new micro- and nanoARPES branch at the ASTRID2 synchrotron light source at Aarhus University in Denmark to visualize the electronic states of twisted graphene layers integrated in device architectures. Specifically, we reveal the flat bands in twisted bilayer and double-bilayer graphene around the magic angles and systematically track the evolution of hybridization effects and moiré bands with small twist angles up to 6°. The interactions in the systems are further tuned by in situ electrostatic doping using a back-gate electrode. Our study paves the way for directly engineering band structure and correlation effects in twisted two-dimensional materials.

O 53.5 Wed 16:15 MA 005

Direct Mn implantation into graphene on Cu(111) substrate: understanding defect production in 2D materials from first-principles calculations — •Silvan Kretschmer[1], Renan Villarreal[2], Lino M. C. Pereira[2], and Arkady V. Krasheninnikov[1] — [1]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden 01328, Germany — [2]Quantum Solid State Physics, KU Leuven, 3001 Leuven, Belgium

Defects influence the properties of 2D materials tremendously, as they essentially consist of surface-only. Contrary to what their name implies, defects not only have detrimental effects, but also are introduced to tune the magnetic, electronic and optical response of 2D materials. The defect induced changes in the material and the concentration of defects produced, e.g by ion irradiation can be rationalized using first-principles calculations [1,2]. Here, we report on our recent simulation results obtained in collaboration with an experimental group on the probability to dope graphene with Mn atoms. Specifically, using ab-initio molecular dynamics we calculated the formation probability of Mn substitutional impurities in graphene on Cu(111) substrate under low-energy ion irradiation.

[1] S. Kretschmer, et.al, ACS Appl. Mater. Interfaces 10 (36), 30827–30836 (2018)

[2] S. Kretschmer, et. al, J. Phys. Chem. Lett. 13, 514–519 (2022)

O 53.6 Wed 16:30 MA 005

Investigating swift heavy ion induced defects in graphene and MoS$_2$ on SiO$_2$/Si via Raman spectroscopy — •Kevin Vomschee[1], Yossarian Liebsch[1], Leon Lasnig[1], Osamah Kharsah[1], Lars Breuer[1], Henning Lebius[2], Abdenacer Benyagoub[2], Clara Grygiel[2], and Marika Schleberger[1] — [1]Faculty of Physics and CENIDE, University of Duisburg-Essen, Duisburg, Germany — [2]CIMAP/GANIL, Caen, France

In the past years, ions have been used as a tool for the so-called defect engineering of 2D materials such as graphene and single-layer molybdenum disulfide (MoS$_2$). The potential impact of swift heavy ion irradiations on strain or doping in 2D materials and, in the case of graphene, also on defect formation can be effectively characterized using Raman spectroscopy. The irradiation of graphene on SiO_2/Si substrates with 91 MeV $^{129}Xe^{23+}$ and 967 MeV $^{129}Xe^{43+}$ at GANIL creates a so called D-peak indicating the presence of defects. The area ratio of the D-peak to the G-peak, another Raman peak that is not defect dependent, is recorded for accumulated ion fluences of up to $2.5{\cdot}10^{13}\mathrm{cm}^{-2}$. Our Raman spectroscopy measurements show that swift heavy ion-induced defects in graphene are smaller in size than those investigated in earlier experiments by highly charged, slow Xe ions and keV Ar^{+} irradiation. We also observed that the 91 MeV $^{129}Xe^{23+}$ ion beam does not significantly change strain or doping of CVD-grown MoS_2 monolayers on a similar substrate for fluences of up to $4{\cdot}10^{12}\mathrm{cm}^{-2}$, but sputters away the monolayer at a fluence of $2.5{\cdot}10^{13}\mathrm{cm}^{-2}$. The fluence dependent sputtering can be observed in a decaying intensity of the spectra.

O 53.7 Wed 16:45 MA 005

Hyperlens enabled defect imaging in hBN-covered few-layer graphene — •Lina Jäckering, Konstantin G. Wirth, and Thomas Taubner — I. Institute of Physics (IA), RWTH Aachen University

Most of the unique phenomena of few-layer graphene (FLG) can only be observed when the FLG flake is encapsulated in hexagonal Boron Nitride (hBN) [1]. The fabrication process of encapsulated graphene devices can alter the stacking order and induce defects within the FLG flake [2]. The present stacking order and possible defects significantly influence the graphene sample's electronic properties. Therefore, the visualization of stacking domains and defects in graphene flakes before, during, and after the fabrication of a transport device is of great interest. Here, we show that scanning near-field optical microscopy (s-SNOM) can visualize submicrometer-sized defects in FLG below 33 nm hBN. We attribute the achieved super-resolution imaging of buried defects to the hyberbolic nature of hBN [3]. hBN hosts hyperbolic phonon polaritons that enable super-resolution focusing through a cover layer of hBN, the so called hyperlensing effect [3]. Here, we present the first practical application of the hyperlensing effect in a hBN-FLG heterostructure. Our work paves the way for characterization of FLG devices during fabrication. [1] Dean et al. Nat. Nanotechnol. **5**, 722 (2010). [2] Geisenhof et al. ACS Appl. Nano Mater. **2**, 6067 (2019). [3] Li et al. Nat. Commun. **6**, 7507 (2015).

O 53.8 Wed 17:00 MA 005

Alkali metal (AM) adsorption on pristine and defective graphite surfaces — •Jafar Azizi, Holger Euchner, and Axel Gross — Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany

While carbon derivatives are still the anodes of choice for Li- and post-Li ion batteries, the quest for improving their properties is ongoing. In particular, when considering soft and hard carbon materials the impact of heteroatoms on Alkali metal adsorption and storage is hardly investigated on the atomistic scale. To gain more insight into the underlying mechanisms, a density functional theory-based study of Li, Na, and K adsorption on pristine and defective graphite surfaces, considering different heteroatom impurities (such as N, S, Si, and O), has been performed. Our results show that on the surface of pure graphite,the adsorption of Li and K ions is energetically more favorable as compared to Na ions. However, in the presence of defects and impurities, Na adsorption also becomes feasible. In general, AM adsorption in the vicinity of defects and impurities is largely favored, putting constrain on the number of AM atoms that participate in charge/discharge processes.

O 53.9 Wed 17:15 MA 005

Enhancement of graphene phonon excitation by a chemically engineered molecular resonance — Xiaocui Wu[1], •Nicolas Néel[1], Mads Brandbyge[2], and Jörg Kröger[1] — [1]Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany — [2]Center of Nanostructured Graphene, Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

The abstraction of pyrrolic hydrogen from a single phthalocyanine on graphene turns the molecule into a sensitive probe for graphene phonons. The inelastic electron transport measured with a scanning tunneling microscope across the molecular adsorbate and graphene becomes strongly enhanced for a graphene out-of-plane acoustic phonon mode. Supporting density functional and transport calculations elucidate the underlying physical mechanism. A molecular orbital resonance close to the Fermi energy controls the inelastic current while specific phonon modes of graphene are magnified due to their coupling to symmetry-equivalent vibrational quanta of the molecule. Funding by the Deutsche Forschungsgemeinschaft through Grant No. KR 2912/17-1 is acknowledged.

O 53.10 Wed 17:30 MA 005

Accelerated First-Principles Exploration of Structure and reactivity in Graphene Oxide — •Zakariya El-Machachi, Damyan Frantzov, Nijamudheen Abdulrahiman, and Volker L. Deringer — Department of Chemistry, University of Oxford, Oxford OX1 3QR, UK

Graphene oxide (GO) materials are widely studied, and yet their atomic-scale structures remain to be fully understood. Here we show that the chemical and configurational space of GO can be rapidly explored by advanced machine-learning methods, combining on-the-fly acceleration for first-principles molecular dynamics with message-passing neural-network potentials. The first step allows for the rapid sampling of chemical structures with very little prior knowledge required; the second step affords state-of-the-art accuracy and predictive power. We showcase the performance of the method by applying it to a model of a partially disordered GO nanoflake and its thermal evolution. Our work provides a platform for routine, quantum-mechanically accurate, and realistic-scale simulations of diverse carbonaceous materials.

O 53.11 Wed 17:45 MA 005

Let's Go on Graphs: X-ray Absorption Spectroscopy of Graphene Oxide using Graph Neural Networks — •Samuel J. Hall[1], Kanishka Singh[1,2], Qinyuan Zhou[1,2], and Annika Bande[1,3] — [1]Helmholtz-Zentrum Berlin, Germany — [2]Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany — [3]Leibniz Universität Hannover, Germany

Graphene oxide (GO) materials, while promising for various applications, can be difficult to fully understand and predict its properties due to the highly irregular molecular structure arising from several oxygen functionalizations across the surface. X-ray absorption spectroscopy (XAS) experiments and simulations can help provide valuable insight by characterizing the electronic structure of materials. However, there are problems with complex spectra being hard to interpret and the prohibitive computational simulation cost for large extended systems. We have developed a machine learning model utilizing graph neural networks (GNN) based on a database of 319 GO-derivative molecules, consisting of 7984 individual atomic XAS spectra calculated with time-dependent density functional theory (TDDFT), that can accurately simulate XAS spectra at a significant lower cost. We show how the model can learn through either the combined spectra of the GO-derivative molecules or the individual atomic spectra to make predictions based on either the larger global environment or the local atomic environment and can further be applied to larger extended systems.