



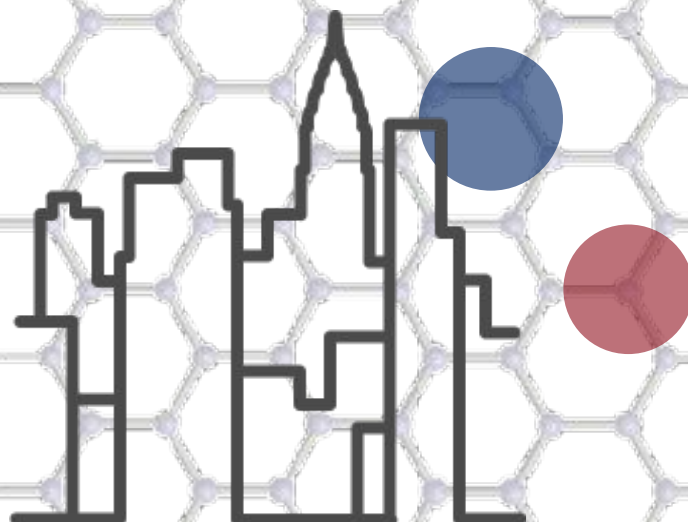
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ABSTRACTS BOOK



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FOREWORD

On behalf of the Organising Committee, we take great pleasure in welcoming you to the 6th edition of the **GrapheneforUS** 2022 International Conference.

GrapheneforUS 2022 online will be a 2 days event that means to gather the key players of the Graphene and 2D Materials Community and related sectors. This event is launched again following the success of the 2018, 2019 & 2020 in-person and the 2021 online editions. **GrapheneforUS** is now an established event attracting global participants and sharing, exchanging, exploring new avenues of graphene and 2DM related scientific and commercial developments.

We truly hope that **GrapheneforUS** 2022 serves as an international platform for communication between science and business.

We are indebted to the following Scientific Institutions and Companies for their help and/or financial support: PennState (Materials Research Institute) / Center for 2-Dimensional and Layered Materials (2DLM) / 2D Crystal Consortium, Columbia University, Texas Instruments and HONDA Research Institute.

We also would like to thank all the speakers and participants that join us this year.

One thing we have for granted: very few industries, one way or another, will escape from the influence of Graphene and 2D Materials and the impact on businesses is here to stay.

Hope to see you again in the next edition of **GrapheneforUS** to be held in 2023 in-person.

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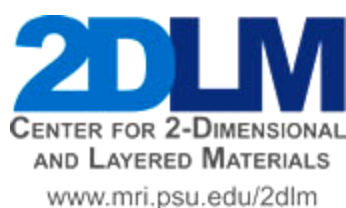
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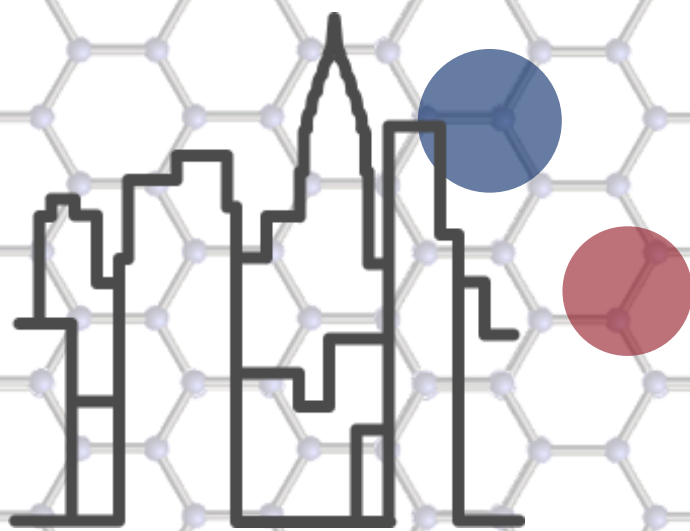
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PLENARY SPEAKERS

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2D Materials for Mass Production

Two-dimensional (2D) materials are ultrathin crystalline nanomaterials with a single layer of atoms with a high degree of anisotropy. 2D materials including graphene have drawn many attentions in semi-conducting industry because they have been considered as one of the candidate materials to overcome the limitation of Si technology beyond 5 nm node.[1] 2D materials research at SAIT has been progressing in two directions. For near term research, we explored 2D materials to enhance the performance of Si technology as interface materials, and for long term we looked into new potential applications. We have confirmed that 2D materials can be used as components of Si devices to improve these properties. [2][3] In pursuit of these research directions, we are investigating a wide range of technologies, from wafer scale 2D material growth to device fabrication. [4][5][6] In this presentation, we will review and discuss the issues and the progresses to apply 2D materials into CMOS devices.

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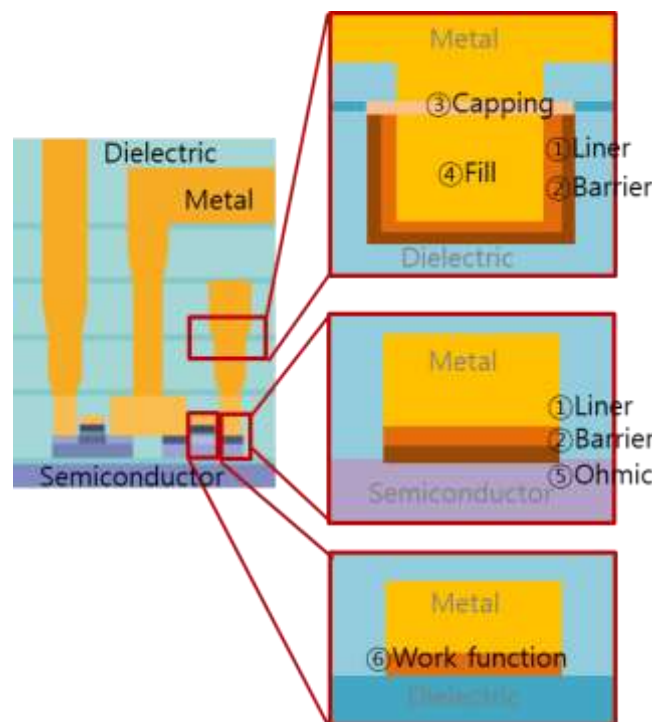


Figure 1: Potential Applications of Graphene for CMOS devices

Klaus Müllen

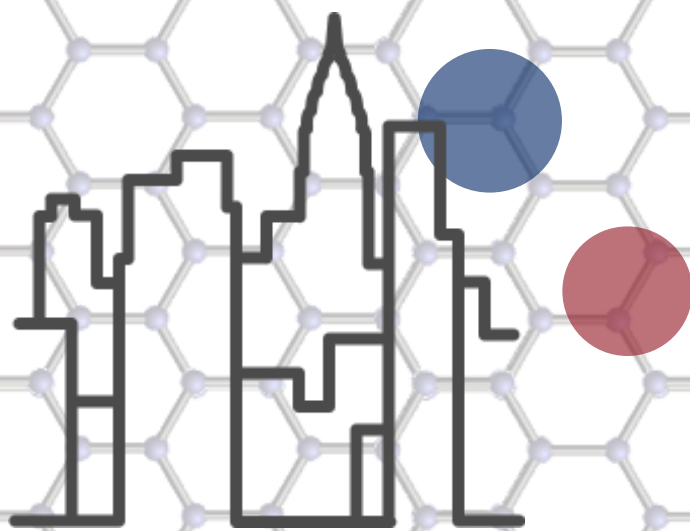
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Graphene and Graphene Nanoribbons

The key breakthrough is the synthesis of graphene nanoribbons (GNRs), quasi-1D-semiconductors, which emerge as unique carbon nanostructures and versatile materials for electronics, optics and energy technology. Their band structures can be widely tuned yielding semiconductors and even topological insulators. The most important features are i) the opening of a band gap due to the geometric confinement, a major difference from graphene, and ii) the occurrence of edge localized electronic states with spin polarization.

All characteristics offer new technological opportunities, for example, adding the spin degree of freedom to graphene-based circuitry or pushing the power density for energy storage in supercapacitors. Comparing materials performances of graphene and graphene nanoribbons is most revealing.



KEYNOTE SPEAKERS

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Quantum devices in graphene

Today's transistors are made of silicon. Also spin qubits in silicon are among the contenders for a future quantum information processor. Graphene has emerged as a unique material in terms of tunability and electronic properties. How can the thinness of graphene be utilized for quantum devices? What can we learn from the peculiar bandstructure of graphene, in particular topological properties such as Berry curvature? In what way does twisting of graphene layers open completely new avenues?

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Two-Dimensional Semiconductors for Logic, Memory and Metamaterials

The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. While a tremendous amount of research activity has occurred in assembling disparate 2D materials into “all-2D” van der Waals heterostructures and making outstanding progress on fundamental studies, practical applications of 2D materials will require a broader integration strategy. I will present our ongoing and recent work on integration of 2D materials with 3D electronic materials to realize logic switches and memory devices with novel functionality that can potentially augment the performance and functionality of Silicon technology. First, I will present our recent work on gate-tunable diode¹ and tunnel junction devices² based on integration of 2D chalcogenides with Si and GaN. Following this I will present our recent work on non-volatile memories based on Ferroelectric Field Effect Transistors (FE-FETs) made using a heterostructure of MoS₂/AlScN^{3, 4} and I also will present our work on Ferroelectric Diode devices also based on thin AlScN.⁵

Next, I will present our work on light-trapping in excitonic systems⁶ and making metamaterials from them.^{7,8} I will present the effect of nano-structuring on hybridization between excitons, plasmons and cavity photons⁷ and will extend this concept to artificial excitonic metamaterials⁸, I will end by giving a broad perspective on future opportunities of 2D and other low-dimensional materials in basic science and applied microelectronics technology.

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Deterministic wafer-scale growth and transfer of single-domain 2D materials

2D material-based devices have received great deal of attention as they can be easily stacked to obtain multifunctionality. With their ultrathin thicknesses, such multifunctioning devices become so flexible and conformal that they can be placed onto any 3D featured surfaces. However, 2D heterostructures are typically demonstrated as stacked flakes where single or few devices can be fabricated due to lack of strategies for layer-by-layer stacking of 2D materials at the wafer scale. While the growth technique could form wafer-scale 2D materials, it has been difficult to control monolayer-by-monolayer growths. In this talk, I will discuss about our unique strategy to isolate wafer-scale 2D materials into monolayers and stack them into a heterostructures by using a layer-resolved splitting (LRS) technique [1-2]. In addition, I will introduce our new technique to directly grow monolayer single-domain 2D materials at the wafer-scale and monolayer-by-monolayer growth of 2D heterostructures [3].

While 2D heterostructures promise interesting futuristic devices, the performance of 2D material-based devices is substantially inferior to that of conventional 3D semiconductor materials. However, 3D materials exist as their bulk form, thus it is challenging to stack them together for heterostructures. My group at MIT has recently invented a 2D materials-based layer transfer (2DLT) technique that can produce single-crystalline freestanding membranes from any compound materials with their excellent semiconducting performance [4-5]. I will also introduce my group's 3D heterostructures by stacking various freestanding single-crystalline membranes to obtain new functionality [6].

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Advanced data encryption using two-dimensional materials

Advanced data encryption requires the use of true random number generators (TRNG) to produce unpredictable sequences of bits. TRNG circuits with high degree of randomness and low power consumption may be fabricated by using the random telegraph noise (RTN) current signals produced by polarized metal/insulator/metal (MIM) devices as entropy source. However, the RTN signals produced by MIM devices made of traditional insulators, i.e. transition metal oxides like HfO_2 and Al_2O_3 , are not enough stable due to the formation and lateral expansion of defect clusters, resulting in undesired current fluctuations and the disappearance of the RTN effect. In this talk I will present the fabrication of highly stable TRNG circuits with low power consumption, high degree of randomness (even for a long string of 224-1 bits) and high throughput of 1 Mbit/s by using MIM devices made of multilayer hexagonal boron nitride (h-BN); we also demonstrate their application to produce one time passwords ideal for the internet-of-everything. The superior stability of the h-BN based TRNG is related to the presence of few-atoms-wide defects embedded within the layered and crystalline structure of the h-BN stack, which produces a confinement effect that avoids their lateral expansion and results in stable operation..

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Figures

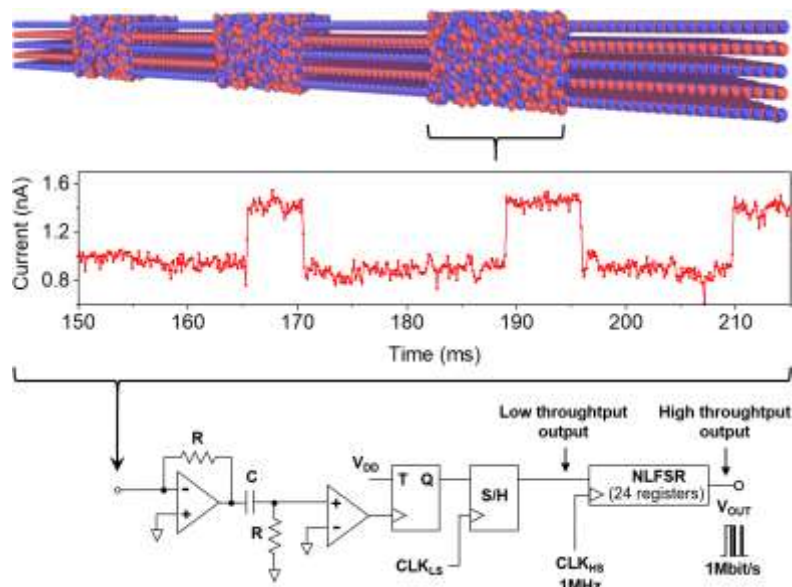


Figure 1: Top-view SEM image of a portion of a 100 x 100 crossbar array of Au/h-BN/Au memristors, each of them with a size of 320 x 400 nm. This is the 2D materials based electronic circuit with a highest number of electronic devices and with a highest integration density ever reported to date

Jia Li

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Flatband, magnetism and superconductivity in twisted trilayer graphene

When layers of graphene are rotationally misaligned by the magic angle, the moiré superlattice induces an extremely flat energy band structure. In such a system, the most prominent Coulomb-driven instability occurs at integer filling and are therefore commonly attributed to spontaneous polarization of the moiré unit cell's 'flavor' degrees of freedom—spin, valley, and the flat-band degeneracy. Flavor polarization at integer filling is thought to crucially determine further instabilities at lower energy scales, such as superconductivity and weaker incompressible states at fractional filling. In this talk, I will examine the unique role of flavor polarization in twisted trilayer graphene and its influence on the interplay between moiré flatband, Coulomb interaction, superconductivity, and ferromagnetism. I will show that such interplay can be modified by tuning experimental knobs including twist angle and proximity effect [1-5]. Our findings shed new light on a variety of quantum phenomena such as superconductivity at low temperature and the strange metal phase at high temperature.

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2D Materials for Industry

Abstract

Semiconductor sales will reach over \$500 billion worldwide in 2021, a gigantic industry that keeps on growing with increasing demand for faster, more powerful, and smaller chips. However, as we keep scaling, the silicon (Si) transistor will soon reach its physical limit, and there is a pressing need to find an alternative post-Si material to enable the continuation of Moore's Law. In the early 2000s, scientists discovered that graphite could be exfoliated down into an atomic form, going from a 3D bulk material down to a 2D stable honeycomb lattice of carbon atoms called graphene. Scientists marveled at graphene's astonishing electrical and mechanical properties, however, for all that graphene has to offer, it lacks a band gap that is essential for logic devices. This created a surge in research on materials beyond graphene, scientists searching for an elusive 2D material that would possess a bandgap to satisfy the need of the semiconducting industry. Monolayer Transition Metal Dichalcogenides (TMDs) possess the bandgap that graphene lacks, and with the vast variety of TMDs available, coupled with its encouraging electrical properties, make TMDs a promising candidate.

In this talk, I will present some of Intel's published research on 2D materials focusing on TMDs, from synthesis and characterization to innovative applications. I will demonstrate, that in Components Research at Intel, we are continuously looking at ways to improve future technologies, and enable the continuation of Moore's Law.

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Resonance Raman enhancement by the intralayer and interlayer electron-phonon processes in twisted bilayer graphene

Raman spectroscopy is a fundamental tool to study twisted bilayer graphene (TBG) systems since the Raman response is hugely enhanced when the photons are in resonance with transition between vHs and new peaks appear in the Raman spectra due to phonons within the interior of the Brillouin zone of graphene that are activated by the Moire superlattice. These new peaks can be activated by the intralayer and the interlayer electron-phonon processes [1]. In order to study how each one of these processes enhances the intensities of the peaks coming from the acoustic and optical phonon branches of graphene, multiple-excitation Raman measurements were performed in many different TBG samples with twisting angles between 4° and 16° and using several different laser excitation energies in the near-infrared (NIR) and visible ranges (1.39 eV to 2.71 eV). Distinct enhancements of the different phonons of graphene were observed for the intralayer and interlayer processes and results are nicely explained by theoretical calculations of the double-resonance (DR) Raman intensity in graphene by imposing the momentum conservation rules for the intralayer and the interlayer electron-phonon processes [2]. Our results show that the enhancement of the Raman response in all cases is affected by quantum interference and obey symmetry requirements for the DR Raman process in graphene.

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Figures

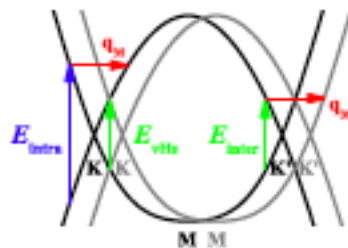


Figure 1: The blue (green) arrow depicts the intralayer (interlayer) electron-phonon process in twisted bilayer graphene

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Exploring Metals at the Atomic Limit

The last decade has seen an exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there is a huge variety of layered materials that range in properties from insulating to superconducting that can be grown over large scales for a variety of electronic devices and quantum technologies, such as topological quantum computing, quantum sensing, and neuromorphic computing. In this talk, I will discuss recent breakthroughs in the realization of unique 2D forms of traditional 3D metals. I will introduce a novel synthesis method, dubbed confinement heteroepitaxy (CHet), that utilizes graphene to enable the creation of atomically thin metals, enabling a new platform for creating artificial quantum lattices with atomically sharp interfaces and designed properties. By shrinking these traditional metals to atomically thin structures, we find that their properties are quite different than their bulk counterparts, lending themselves to unique quantum and optical applications not possible before.

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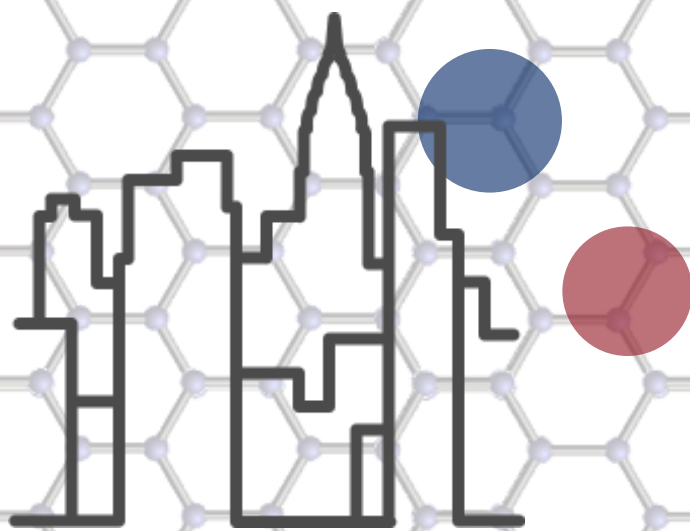
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Strain Resilient versus Strain Reconfigurable Systems in 2D Material Heterostructures

Understanding the mechanical deformability of nanomaterials is critical to realizing a host of next generation technologies like stretchable electronics, reconfigurable quantum states, three dimensional multifunctional surfaces, and nanoscale machines. Due to their unparalleled mechanical strength and stability, two-dimensional (2D) materials like graphene and MoS₂ represent the ultimate limit in size of both mechanical atomic membranes and molecular electronics. One of the most exciting research directions is on how to integrate the outstanding mechanical properties and electronic functionality of 2D materials together. In this presentation, we will: (1) Discuss strategies for designing strain, strain gradients and interfacial slip in 2D materials through nanoscale bends, microscale wrinkling, and deposited stressor layers; (2) Explore the interplay between interfacial friction and slip, mechanical deformability, material strain, and resulting optoelectronic properties; (3) Demonstrate 2D material based stretchable electronics and nanoelectromechanical systems which leverage the electromechanical coupling and interfacial structure to enhance reconfigurability. Taken together, these experiments show that interfacial slip strongly affects the mechanics and electronics of 2D material heterostructures and leads to membranes which are orders of magnitude more deformable than conventional 3D materials.



INVITED SPEAKERS

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2D materials to make perovskite-based photovoltaics competitive with the exiting PV technologies

The winning future of the emerging perovskite solar cells is closely linked to the dimension scalability and the possibility to boost the existing photovoltaic (PV) technology in tandem configuration. Indeed, on one hand, the main limit to the perovskite technology commercialization consists in a drop in power conversion efficiency (PCE) when dimensions are scaled from prototype small-area cell to module configuration. On the other hand, the well-established silicon PV technologies can overcome the Shockley-Queisser limit only when combined in tandem configuration. The synergetic development of large area perovskite devices fitting the standard silicon wafer dimensions and the optimization of perovskite/silicon tandem architectures can definitively open up new horizons for winning the commercialization challenges. To this end, bi-dimensional (2D) materials recently demonstrated their effectiveness in boosting the perovskite PV device efficiency and stability by mitigating the performance drop when scaling the cell dimensions up to module size.^[1] Here, the use of interface engineering based on materials is proposed as an efficient tool for trap passivation and energy level alignment, by mitigating the performance losses induced by the scaling-up process.^[2] In particular, the successful application of 2D materials, i.e., graphene,^{[3][4][5]} functionalized MoS₂,^{[6][7]} and MXenes^{[8][9]} in perovskite solar modules (PSMs) allowed to achieve PCE overcoming 17% and 14.5% over 121 and 210 cm² substrate area respectively.^[10] Moreover, an ad-hoc lamination procedure employing low temperature cross linking EVA (at 80°C-85°C) allowed to fabricate several 0.5 m² panels, finally assembled in Crete Island, in the first worldwide fully operating 2D material-perovskite solar farm. The 2D material optimization developed for opaque device can be easily transferred on semitransparent ones for feasible application in tandem 2T mechanically stacked configuration when coupled with crystalline Silicon (c-Si) technology. Indeed, the possibility to separately optimize the two sub-cells allows to carefully choose the most promising device structure for both top and bottom cells.^[11] More in detail, semi-transparent perovskite top cell performance is boosted through a rational use of additives and bi-dimensional materials to tune the device interfaces and to optimize the light management within the device structure. In addition, a protective buffer layer (PBL) based on MoO₃ thin film is used to prevent damages induced by the transparent electrode sputtering deposition over the hole transporting layer. At the same time, a textured amorphous/crystalline silicon heterojunction (c-Si HTJ) cell fabricated with an in-line production process is used as state of art bottom cell. The tandem perovskite/Si tandem device demonstrates remarkable PCE above 28%. Finally, the scale up of this new tandem configuration is now calling for clever strategies inspired by the already exiting PV technology.

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CMOS integration of graphene for multiplexed sensing

The development of graphene field-effect transistor based biosensing has been fast during the last few years, both in terms of the fabrication scale-up and functionalization towards biorecognition from real sample matrices. The next steps in the industrialization relate to reliability and require increased statistics. In the fabrication, the device-to-device, and batch-to-batch variability need to be addressed, considering especially the stability, doping and contact resistance of the devices. In the functionalization and referencing towards truly quantitative sensors and on-chip bioassays, the improved statistics requires sensor arrays with controlled variability on functionalization. Such multiplexed bioassays, whether based on graphene or on other sensitive nanomaterials, are among the most promising technologies for label-free electrical biosensing.

As one important step towards that, we report wafer-scale fabrication of CMOS integrated graphene FET arrays with high yield and uniformity, designed especially for biosensing applications. We demonstrate the operation of the sensing platform with 512 GFETs in simultaneous detection for sodium chloride salt concentration series. This platform offers a truly statistical approach on graphene FET based biosensing and further on quantitative and multi-analyte sensing and can also be applied on other fields relying on functionalized FETs, such as gas or chemical sensing or IR detection.

Figures

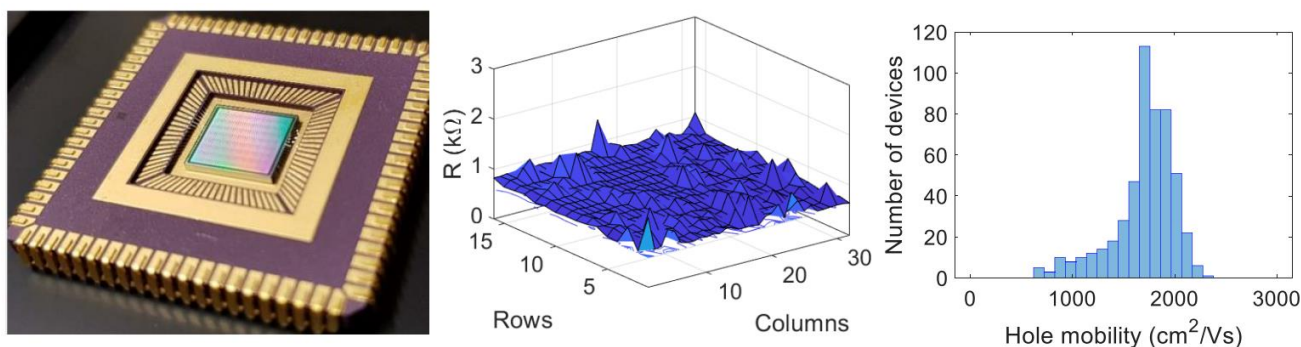


Figure 1: (Left) CMOS-integrated biosensor chip wire bonded on the chip carrier; (Middle) Resistance map of biosensor pixels on one chip with zero bias (Right) Histogram of hole mobility measured from an array of 512 graphene biosensors on a single silicon CMOS chip.

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2D materials: from safety to immune-engineering

Two dimensional materials such as graphene and Mxenes are destined to leave an indelible mark in many application areas including biomedicine. In particular, due to a multitude of exceptional intrinsic properties, these materials offer new perspectives for the development of advanced tools for therapeutic delivery approaches, imaging, cancer theranostics, and tissue regeneration or engineering.

For any biomedical applications, the immune system plays a fundamental role. Understanding whether and how immune cells respond to nanomaterials by immune activation or immunosuppression might allow taking advantage of both of those selected intrinsic immune properties. For example, immuneactivation could be useful to stimulate the immune system against malignant cells in cancer immunotherapy or as vaccine adjuvants. On the other hand, immunosuppression may find applications for overactive inflammation in allergic reactions, chronic inflammation, autoimmune disorders, and organ transplantation. Here we present our “Nanoimmunity-by-design concepts” (figure 1.) as well as published and unpublished data on the immune-based applications of graphene, Mxenes and other advanced 2D materials.

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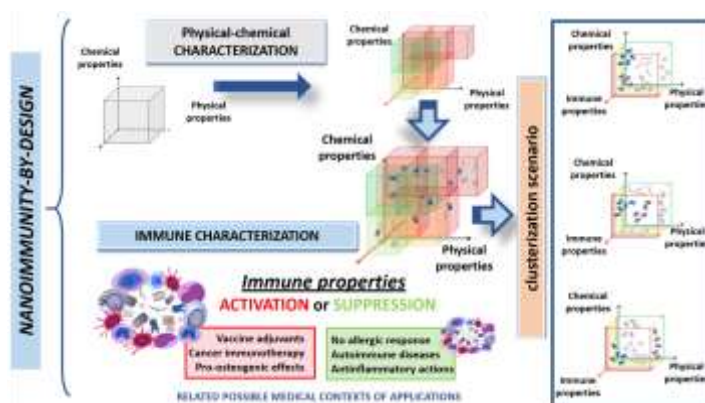


Figure 1: Schematic representation of the Nano-immunity-by design concept

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Dark-exciton driven energy funneling into dielectric inhomogeneities in two-dimensional semiconductors

The optoelectronic and transport properties of two-dimensional transition metal dichalcogenide semiconductors (2D TMDs) are highly susceptible to external perturbation, enabling precise tailoring of material function through post-synthetic modifications. Here we show that nanoscale inhomogeneities known as nanobubbles can be used for both strain and, less invasively, dielectric tuning of exciton transport in bilayer tungsten disulfide (WSe₂). We use ultrasensitive spatiotemporally resolved optical scattering microscopy to directly image exciton transport, revealing that dielectric nanobubbles are surprisingly efficient at funneling and trapping excitons at room temperature, even though the energies of the bright excitons are negligibly affected. Our observations suggest that exciton funneling in dielectric inhomogeneities is driven by momentum-indirect (dark) excitons whose energies are more sensitive to dielectric perturbations than bright excitons. These results reveal a new pathway to control exciton transport in 2D semiconductors with exceptional spatial and energetic precision using dielectric engineering of dark state energetic landscapes [1].

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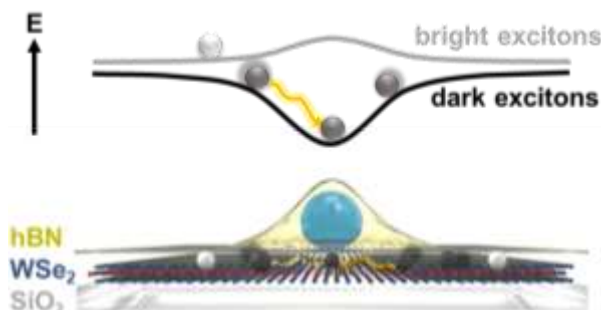


Figure 1: Dark excitons are funneled in dielectric inhomogeneities.

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Direct growth of sub-10nm MoS₂ nanoribbons and their width dependent quantum properties

Many of the electronic and optical behaviors of atomically thin transition metal dichalcogenides are strongly dependant on their number of layers and width. Therefore, it is of central importance to develop facile methods for their controllable synthesis. We report the growth of bilayer MoS₂ nanoribbons enabled by nickel nanoparticles, which promotes both heterogenous nucleation of the first layer of MoS₂ and simultaneously catalyzes homoepitaxial tip-growth of a second layer via vapor-liquid-solid (VLS) mechanism, resulting in bilayer nanoribbons with width controlled by the nanoparticle diameter. Theoretical simulations also confirm the VLS growth mechanism towards nanoribbons and its orders of magnitude higher growth speed compared to the conventional non-catalytic growth of flakes. Coulomb blockade oscillations are observed in the transfer characteristics of the nanoribbons at low temperatures. Such an oscillation behavior is width-dependent, only showing in nanoribbons with width <20 nm, and observable at temperatures up to 80 K. The phenomenon evidences the value of this proposed synthesis strategy for future nanoelectronics and quantum applications.

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Figures

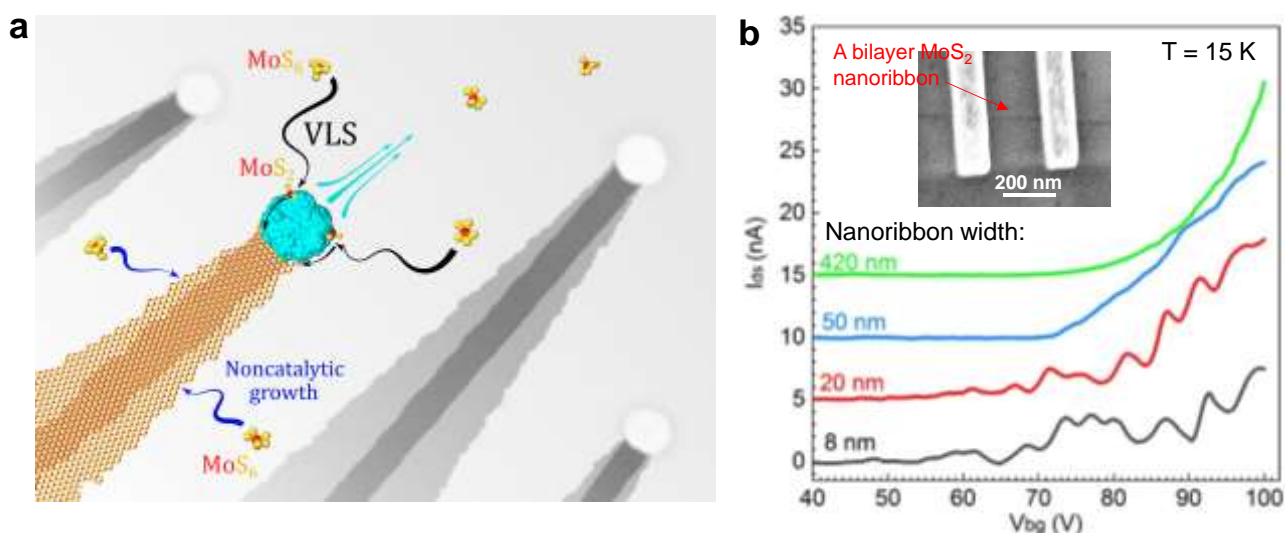
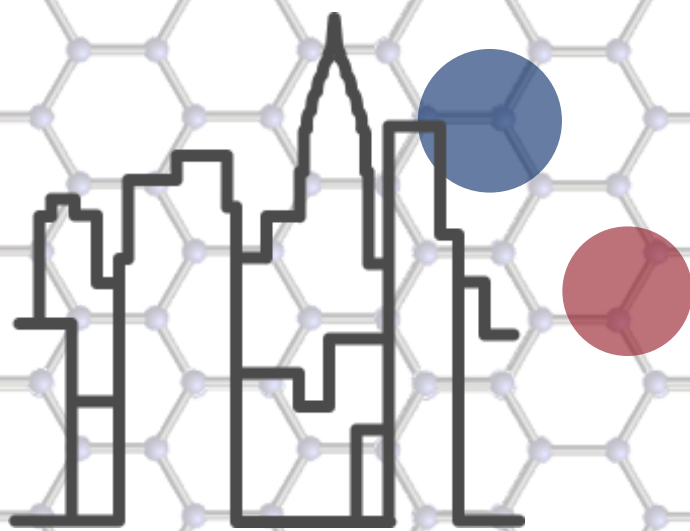


Figure 1: (a) Schematic illustration of the bidirectional growth of the bilayer MoS₂ ribbons (top layer: VLS, bottom layer: non-catalytic). (b) Transfer curves of nanoribbons with different widths (420–8 nm) at 15 K. The nanoribbons width with <20 nm show strong Coulomb blockade oscillations. Inset is the SEM image of a typical device.



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Different molecular interactions of graphene sheet and quantum dot nanomaterials

Thanks to its extraordinary properties, graphene attracts much research and applications interest. The rich π -system and high surface area of graphene are attractive for non-covalent interactions, but their structural and electronic nature is complex and remains unclear, particularly in solvents including water. Hydrophobic and π - π stacking interactions are often reported as their driving force [1, 2], but the nature of interaction may be misunderstood from surface characterisation and computational modelling done in the absence of water. Where water has been included in fewer studies, very different behaviour is reported [3, 4]. Here, we investigated the molecular nature of interactions of graphene sheets and quantum dots in water using NMR spectroscopy, and develop a mechanistic model to explain the major differences in interactions revealed. Self-assembly of aromatic compounds is revealed by large upfield shifts of ^1H NMR signals due to the orbital diamagnetism of aromatic ring currents. The large orbital diamagnetism of graphene aligns planar π - π assembly in the magnetic field and thereby depletes signals without shift, whereas remaining signals are un-shifted but broadened (Figure 1), indicating unaligned non-planar association with graphene and different interactions of chemically-diverse structures with graphene surfaces and edges. As the size and orbital diamagnetism of graphene decreased into quantum dots with greater disorder, planar and non-planar molecular interactions were markedly less.

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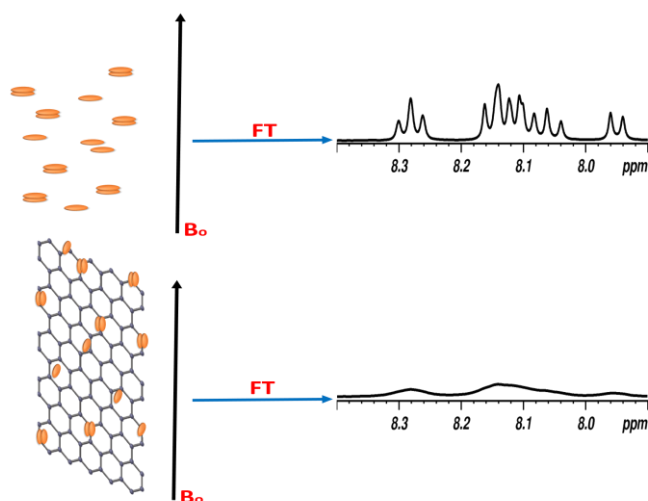


Figure 1: Effect of graphene on ^1H -NMR spectra. Chemical shifts of ^1H protons of aromatic compounds in the absence (top) and presence (bottom) of graphene.

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Innovative Graphene Hall Effect Sensor for Extreme Temperatures

Łukasiewicz Research Network – Institute of Microelectronics and Photonics has developed the construction and technology of an innovative graphene-based magnetic field sensor.

The sensor is based on hydrogen-intercalated quasi-free-standing graphene epitaxially grown on semi-insulating silicon carbide using the Chemical Vapor Deposition method [1,2,3]. It is environmentally protected by atomic-layer-deposited aluminum oxide passivation.

Graphene's quality and the sensor's device technology is monitored by means of Raman spectroscopy, SIMS, spectroscopic ellipsometry, high-resolution XRR, SEM, AFM, high-resolution photo-induced transient spectroscopy and Hall effect measurements between the temperature of liquid nitrogen and 770 K.

The device comes in two variants. The one on semi-insulating vanadium-compensated on-axis 6H-SiC(0001) offers current-mode sensitivity of 140 V/AT within the temperature range between liquid nitrogen and 573 K [4], the other one on semi-insulating high-purity on-axis 4H-SiC(0001) offers 80 V/AT but up to 770 K [5].

The sensor holds promise for application in brushless electric motors, electric current sensors and magnetic field detectors operating under high temperatures and neutron irradiation [6]. Potential areas of competitive advantage include electric vehicles, charging stations, smart metering, high-temperature electronics and magnetic field confinement fusion reactors.

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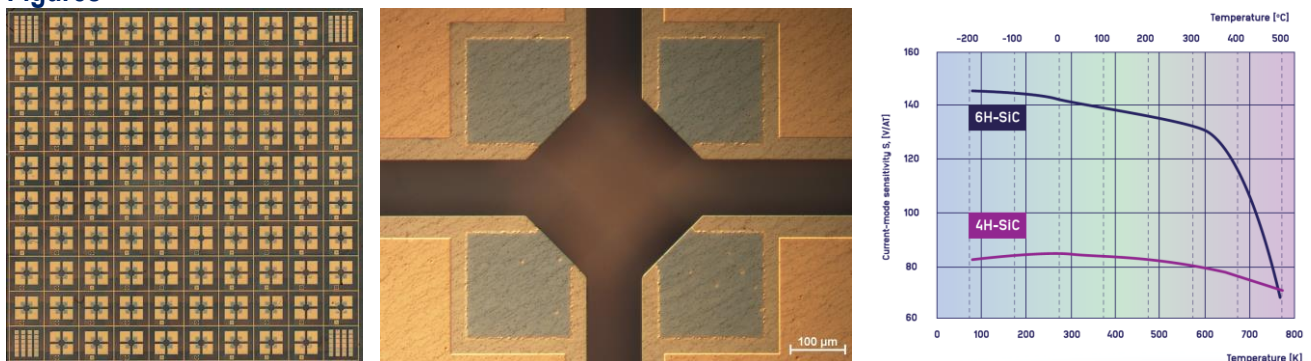


Figure 1: Optical image of the Hall effect sensor and a temperature profile of its current-mode sensitivity

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An Innovative Approach for Wafer Scale High Optical Quality TMDs Atomic Layers Growth by MOCVD Technique

Abstract

The successful growth of Two-Dimensional (2D) TMDs materials is one of the prerequisites in order to take advantage of their remarkable electronic and optoelectronic properties in real applications. This requires the systematic study of the growth mechanism of such atomic films. Here, I will present the results on the growth of WS₂ and WSe₂, via the metal-organic chemical vapor deposition (MOCVD) approach. One of the major advantages of MOCVD is the use of volatile precursors for both, the metal and the chalcogen sources, in contrast to the more common metal oxide powder-based CVD approach [1], where the control over the precursor supply is limited. Although the MOCVD method results in large-scale growth, it might include intrinsic carbon contamination [2] arising from the volatile organic-based precursors themselves. This, together with the high rate of precursor decomposition at the growth temperature, leads to the formation of nano-crystalline films. Here, a Growth-Etch cycle technique is developed, in which the precursors are sequentially delivered while a small amount of water vapor is introduced to the growth chamber. This causes the re-evaporation of small and defective domains as well as the carbon contaminants from the growth substrate, allowing the highly crystalline domains to expand, resulting in high-optical quality large domains or continuous atomic layers, depending on growth conditions [4]. This methodology could be further extended to other 2D materials in general and TMDs in particular. Finally, I will describe how the MOCVD approach can be used to study the van der Waals epitaxy of TMDs on different substrates.

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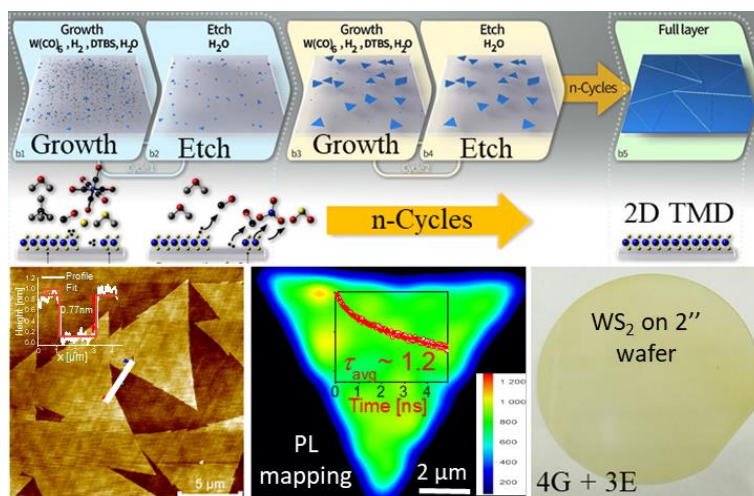


Figure 1: Schematic model of the growth-etch method, Topography map with the corresponding height profile of a monolayer WS₂, PL intensity map and TRPL decay measurement on a single crystal WS₂, a full coverage monolayer WS₂ on a 2'' sapphire substrate.

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Determining the number of graphene layers based on Raman response of the SiC substrate

In this presentation we demonstrate a method for direct determination of the number of layers of hydrogen-intercalated quasi-free-standing epitaxial Chemical Vapor Deposition graphene on semiinsulating vanadium-compensated on-axis 6H-SiC(0001). The method anticipates that the intensity of the substrate's Raman-active longitudinal optical A_1 mode at 964 cm^{-1} is attenuated by 2.3% each time the light passes through a single graphene layer. Normalized to its value in a graphene-free region, the A_1 mode relative intensity provides a greatly enhanced topographic image of graphene and points out to the number of its layers within the terraces and step edges, making the technique a reliable diagnostic tool for applied research. Raman spectra of graphene and the underlying SiC substrate were obtained in a backscattering geometry of the Renishaw inVia confocal microscope using the 532-nm (2.33 eV) line of a continuous-wave Nd:YAG laser and the Andor Newton CCD detector. The laser power was kept at 13.5 mW and the spot size was reduced to $0.3\text{ }\mu\text{m}$. For possibly highest imaging resolution the lateral steps in both X and Y directions were set at $0.3\text{ }\mu\text{m}$. In order to extract graphene spectra and the substrate response three types of 4624-point $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ maps were recorded. The authors believe that the protocol brings a reliable diagnostic tool for the quantification and comparison of graphene on SiC properties, thus accelerating research and development activities in the field of graphene-based applications.

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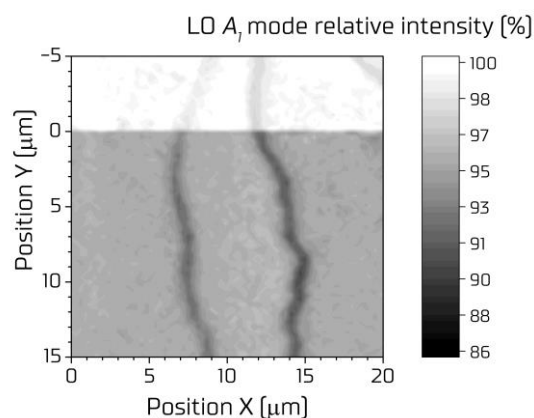


Figure 1: High-resolution Raman map of the 6H-SiC longitudinal optical (LO) mode relative intensity at 964 cm^{-1} .

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MXene-mediated immune cell-cell interactions revealed by enzymatic LIPSTIC labeling

Among two-dimensional nanomaterials, the transition metal carbides/carbonitrides (MXenes) [1] have gained remarkable attention for their potential as biomedical nanotools [2, 3]. Due to their unique physicochemical properties, MXenes enable a wide range of biomedical applications. The use of MXenes was recently explored to fight against SARS-CoV-2, demonstrating the immune-modulatory properties of Ti_3C_2 MXene [4, 5]. The comprehension of the biomolecular effects of MXenes on immune cells is a prerequisite for their exploitation in future translational applications. To characterize the complex interactions between MXenes and immune cells, we applied the Labelling Immune Partnerships by SorTagging Intercellular Contacts (LIPSTIC) [6] approach to nanomaterials (LIPSTIC). A key phenomenon in the immune response, the intercellular communication between T cells and antigen-presenting dendritic cells (DCs), was investigated after exposure to two highly stable and well-characterized MXenes: V_4C_3 and Ti_3C_2 . Cell-specific intercellular communication between DCs and T cells was drastically decreased by the former, which induced immunosuppression. Moreover, the anti-inflammatory activity of V_4C_3 was revealed by functional analyses and cytokine quantification. Our results open the way for i) new investigations on the promising immunomodulatory properties of novel MXenes in the context of autoimmune diseases and ii) a novel methodological approach in nanotoxicology and nanomedicine.

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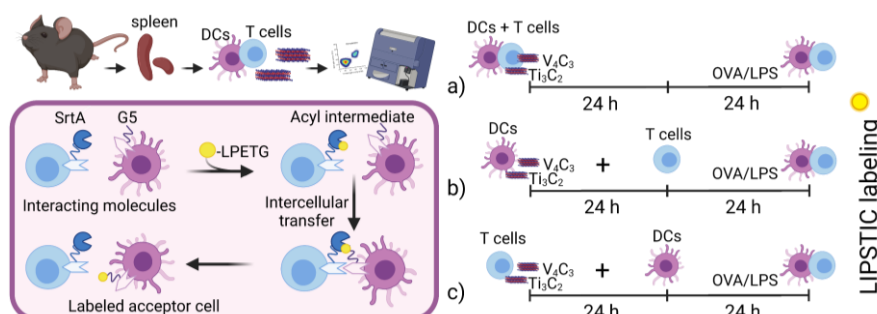


Figure 1: Ex vivo tracking of ligand-receptor interactions using LIPSTIC. Schematic representation of the LIPSTIC approach. Ligand and receptor of interest are genetically fused to either Sortase A (SrtA) or a tag consisting of five N-terminal glycine residues (G5). The loading of a biotinylated LPETG peptide onto SrtA substrate leads to the formation of an acyl intermediate. When ligand and receptor interact, SrtA catalyzes the substrate transfer onto the G5-tagged receptor. After cells separate, the interaction is revealed by the biotinylated label on the surface of the G5-expressing cell (left panel). The LIPSTIC labeling of T cell - DCs interactions was performed as described in the right panel.

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Active thermography for the analysis of graphene

A large variety of methods exists to analyze mostly inorganic engineered nanoparticles (NPs) in dispersions, as thin films or embedded (e.g. in nanocomposites). However, many standard analyses (e.g. chemical analysis) fail when it comes to carbon-based nanomaterials and the analysis often requires complicated sample preparation (e.g. microtome cutting) or labelling.

Methods used to detect and quantify carbon-based nanomaterials or analyze their size, size distribution, and colloidal state in analytically complex environments (e.g. cell culture media, serum) like dark-field hyperspectral imaging, electron microscopy or dynamic light scattering require complex and time-consuming sample preparation, are lacking spatial information and only analyze a small portion of the sample. Additionally, the quantification of carbon nanomaterials is even more challenging and methods for their quantification are simply missing.

Carbon nanomaterials have the ability to produce heat upon external stimulation by absorbing and scattering light [1], [2].

In this talk I will present a new technique based on lock-in-thermography (LIT) to measure and quantify the heat produced by carbon nanomaterials upon light stimulation. This heat can be recorded with an infrared camera and is processed by a specially developed LIT algorithm to yield 2D-images for analyzing carbon nanomaterials. The advantage of this set-up is the fast and accurate analysis of carbon nanomaterials in a variety of matrices, without requiring complicated sample preparation. Additionally, the method can be used for semi-quantitative analysis [3], [4].

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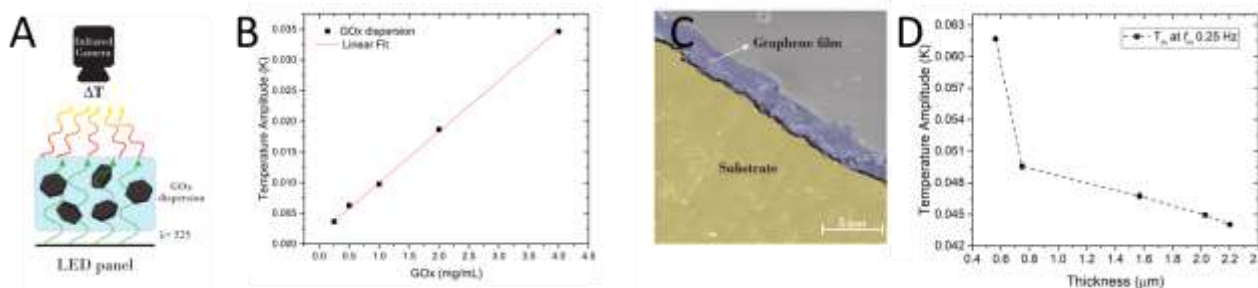


Figure 1: A: Measurement principle; B: Measurement of the average heating signal versus graphene oxide concentration; C: Graphene film on polymer substrate; D: Film thickness versus average heating signal

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Investigation of graphene on SiC under neutron irradiation by Raman Spectroscopy

In this work, we report study on the impact of neutron radiation on quasi-free-standing (QFS) graphene [1]. For this purpose, we have fabricated hydrogen-intercalated QFS graphene on semiinsulating high-purity 4H-SiC (0001) [2], passivated with an Al_2O_3 layer [3], and exposed it to a fast-neutron fluence of $\approx 6.6 \times 10^{17} \text{ cm}^{-2}$. The result have shown that the graphene sheet is only moderately affected by the neutron radiation with the estimated defect density of $\approx 4 \times 10^{10} \text{ cm}^{-2}$. The effect was more pronounced within the SiC step edges than the terraces [4]. However, in both cases the defect density was seven orders of magnitude lower than the fluence, which indicates that graphene has a small cross-section for neutrons.

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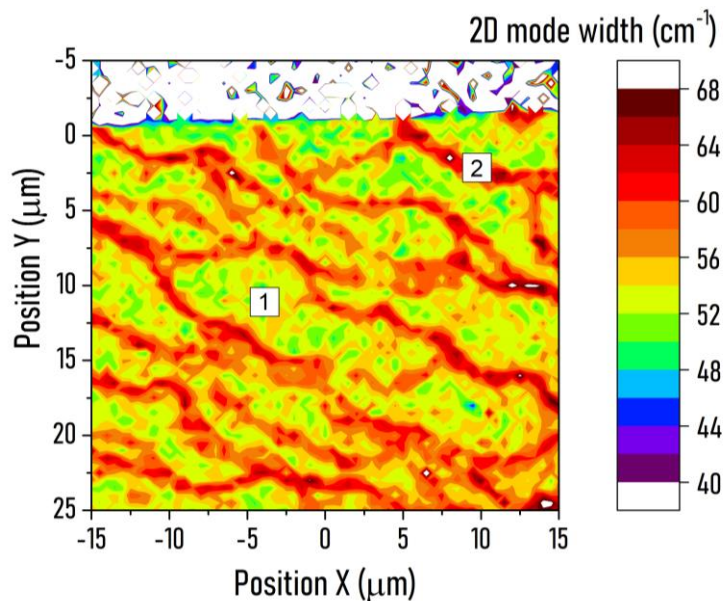


Figure 1: High-resolution post-neutron-irradiation Raman map (2D band width) of hydrogen-intercalated QFS epitaxial CVD graphene on semiinsulating high-purity on-axis 4H-SiC (0001), all passivated with a 100-nm-thick-atomic-layer-deposited aluminum oxide layer. Spots numbered 1 and 2 have their individual Raman spectra.

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Folding and fracture of graphene grown on a Cu(111) foil

A single-crystal graphene film grown on a Cu(111) foil by chemical vapor deposition (CVD) has ribbon-like fold structures. These graphene folds are highly oriented and essentially parallel to each other.^[1] We found Cu surface steps underneath the graphene are along the $\langle 110 \rangle$ and $\langle 211 \rangle$ directions, leading to the formation of the arrays of folds. The folds in the single-layer graphene (SLG) are not continuous but break up into alternating patterns. A “joint” (an AB-stacked bilayer graphene) region connects two neighboring alternating regions, and the breaks are always along zigzag or armchair directions. We are able to *perfectly* reproduce the structures of the fractured folds by paper kirigami. Once we learned this we realized we can present a really clear picture about how the graphene is fractured that consists of several steps including wrinkling, initiation of cracks, propagation of cracks during folding over, and sliding-induced further propagation of cracks. Folds formed in bilayer or few-layer graphene are continuous with no breaks. Molecular dynamics simulations show that SLG suffers a significantly higher compressive stress compared to bilayer graphene when both are under the same compression, thus leading to the rupture of SLG in these fold regions. The fracture strength of a CVD-grown single-crystal SLG film is simulated to be about 70 GPa.^[2] We appreciate support from Institute for Basic Science (IBS-R019-D1).

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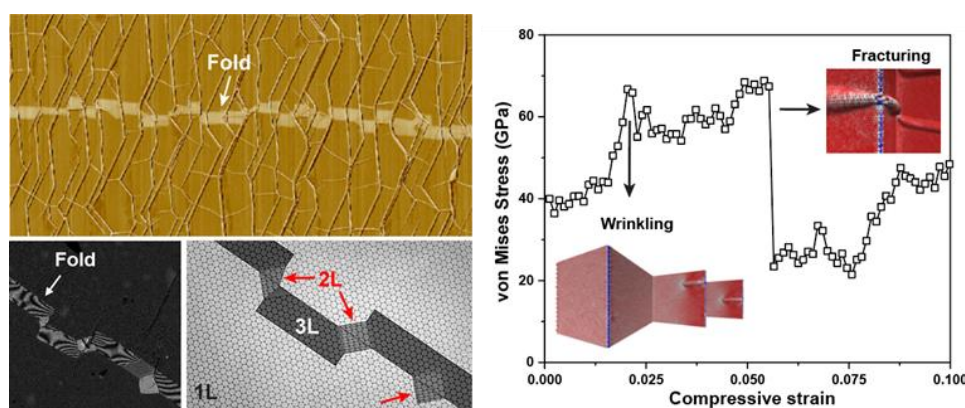


Figure 1: The structure of fold and molecular dynamics simulations showing the fracture of fold.

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Phonon limited mobility in h-BN encapsulated AB-stacked bilayer graphene

We report the electrical transport in h-BN encapsulated AB-stacked bilayer graphene theoretically and experimentally. Using the perturbation theory within the tight-binding model approach, we identify the dominant role of the shear phonon mode scattering on the carrier mobility in AB-stacked graphene bilayer at room temperature. The shear phonon mode is absent in free-standing monolayer graphene, which explains high mobilities in monolayer devices fabricated under similar conditions resulting in minimal Coulomb impurity scattering. At temperatures above 200K, the surface polar phonon scattering from boron-nitride (BN) substrate contributes significantly to the experimental mobilities of 15,000 -20,000 cm^2/Vs at room temperature, and carrier concentration $n \sim 10^{12} \text{ cm}^{-2}$ reported here. A screened SPP potential for a dual encapsulated bilayer and transferable tight-binding model allows us to predict mobility scaling with temperature and bandgap for both electrons and holes in agreement with the experiment.

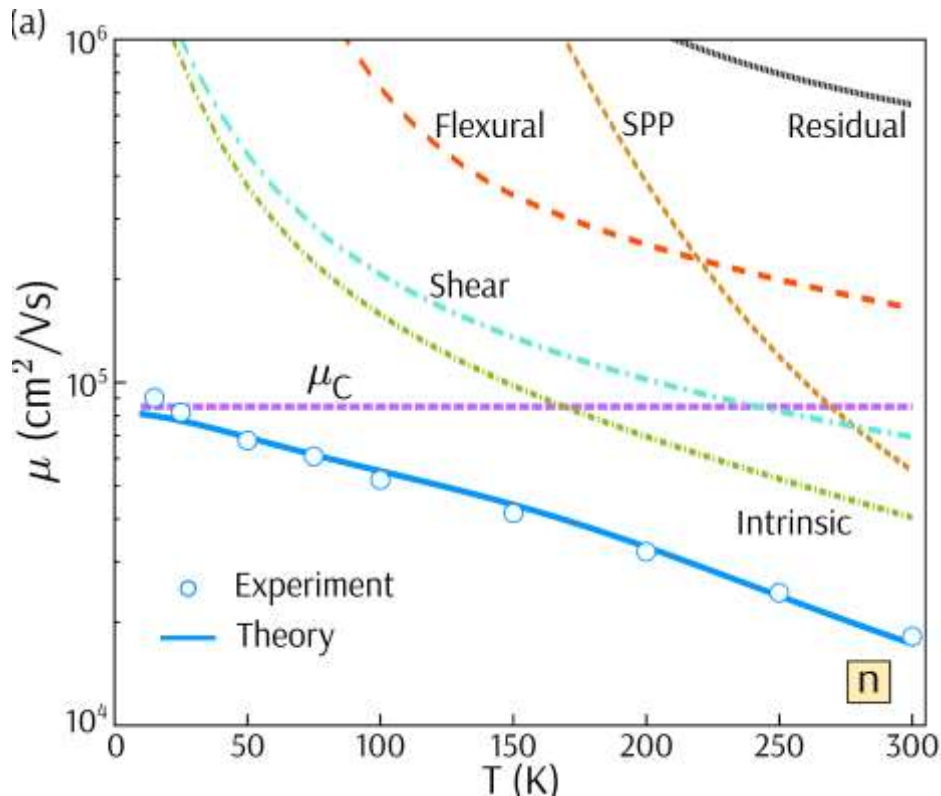


Figure 1: Overall experimentally measured and theoretically calculated electron mobilities as a function of temperature (blue circles and blue curve, respectively), at electron carrier density $0.9 \times 10^{12} \text{ cm}^{-2}$. The theoretical intrinsic, SPP, shear, flexural, and residual phonon-limited mobilities are shown by the dashed curves (from bottom to top at room temperature, respectively).

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Enhancement of graphene-related and substrate-related Raman modes through dielectric layer deposition

In this work, we demonstrate a method for the enhancement of Raman active modes of hydrogen-intercalated [1] quasi-free-standing epitaxial chemical vapor deposition graphene and the underlying semi-insulating 6H-SiC(0001) substrate through constructive signal interference within atomic-layer-deposited amorphous Al₂O₃ passivation. We find that an optimum Al₂O₃ thickness of 85 nm for the graphene 2D mode and one of 82 nm for the SiC longitudinal optical A₁ mode at 964 cm⁻¹ enable a 60% increase in their spectra intensities. We demonstrate the method's efficiency in Raman-based determination of the dielectric thickness and high-resolution topographic imaging of a graphene surface [2,3].

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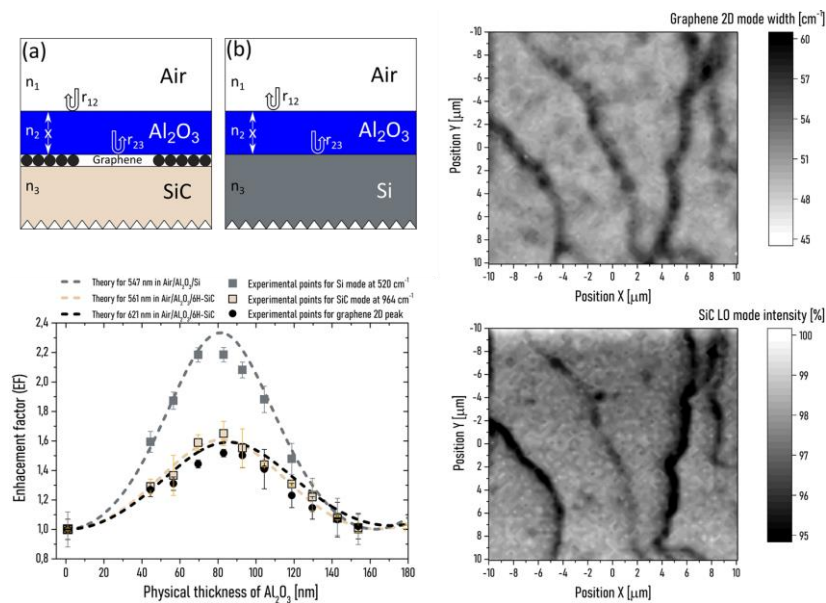


Figure 1: Schematic of the two considered systems. Theoretical and experimental enhancement factor (EF) for the SiC LO A₁ mode, the Si mode and the QFS graphene 2D mode all as a function of the Al₂O₃ physical thickness. High-resolution Raman map of hydrogen-intercalated QFS epitaxial CVD graphene on semiinsulating vanadium-compensated on-axis 6H-SiC(0001) passivated with 69-nm-thick Al₂O₃: (a) Graphene 2D mode FWHM. (b) Relative intensity of the SiC longitudinal optical A₁ mode at 964 cm⁻¹ [2].

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A study on defective graphene: correlating Raman and transport measurements, and towards strain effects

Abstract: Although previous studies had reported Raman and weak localization properties of graphene separately, very few studies examined the correlation between Raman and weak localization characterizations of graphene. Here, we report a Raman spectroscopy and low magnetic field electronic transport study of graphene devices with a controlled amount of defects introduced in graphene by exposure to electron-beam irradiation and oxygen plasma etching. The relationship between the defect correlation length, calculated from the Raman “D” peak, and the characteristic scattering lengths computed from the weak localization effects measured in magnetotransport was investigated. Furthermore, the effect on the mean free path length due to increasing amounts of irradiation incident on the graphene device was examined. The dependence of parameters on the increase of irradiation was shown to be related to the increase of disorder through the concomitant decrease in mean free path length. These findings are valuable for understanding the correlation between disorder in graphene and the phase coherence and scattering lengths of its charge carriers. In the next step we will also transfer such defective graphene on ferroelectric substrates such as PMN-PT and we will discuss the potential strain tuning effects and applications.

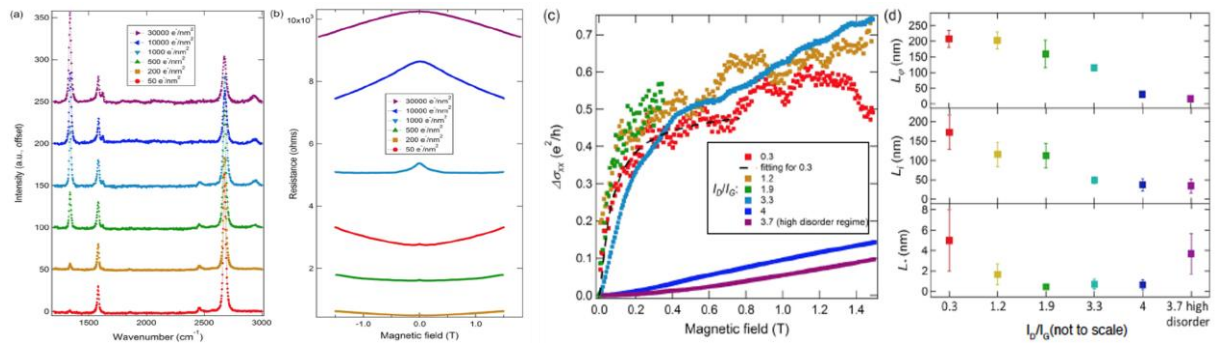


Figure 1: Disorder Induced by e-- Beam Exposure (a) Raman spectra (excitation wavelength 532 nm) of graphene for a progression of accumulated electron-beam exposures show an increase in the disorder-induced ‘D’ peak with increased radiation exposure. The spectra are offset vertically for clarity. (b) Magnetic field versus measured dependent resistance yield symmetric line shapes that notably develop a central resistance peak associated with weak localization (c) Average change in conductivity versus magnetic field for the same progression of accumulated electron-beam exposures which are denoted by their ID/IG ratio derived from part (a). (d) A comparison that shows the decrease of scattering length for low to high disorder samples as indicated by the increasing ID/IG ratio. Weak localization scattering lengths are derived from the conductivity curves in (c).

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Doped Graphene on Silicon FET for High Drain Current and Applications in RF And Logic Circuits

The Si-adsorbed and Si-substituted monolayer Si-doped graphene (Si:Gr) material has a range of structural and electronic features, according to recent researches. The Si:Gr demonstrates adatom-diversified geometric structure, silicon-carbon dominated energy bands, density of states projected from atom's orbit and charge concentration in space. The exploration of these critical physical characteristics generate distinct physical and electrical properties of the distinct material Silicon doped graphene (Si:Gr) permitting it to be used in semiconductor technology [1]. Due to the excellent carrier mobility and saturation velocity, graphene devices are very useful in RF applications. Recent studies suggest that utilizing bare silicon as a supporting substrate without an insulating layer under the graphene channel in conventional field effect transistor (FET), can result in high output resistance and voltage gain, which provides higher cut-off frequency comparing with conventional graphene-FET (GEFT) [2]. In this work, an N-channel GFET with printed channel length of 50nm has been designed with Si:Gr as channel material and the Si:Gr is deposited on lightly doped p-type silicon substrate eliminating the insulator layer. For optimum RF performance bottom gate with SiO₂ as gate dielectric has been utilized. The device has provided maximum cut-off frequency of 496GHz and Ion/Ioff ratio of 139.5x10³ (bottom gate, metallic contact) proposing a novel device for RF and logic circuit applications.

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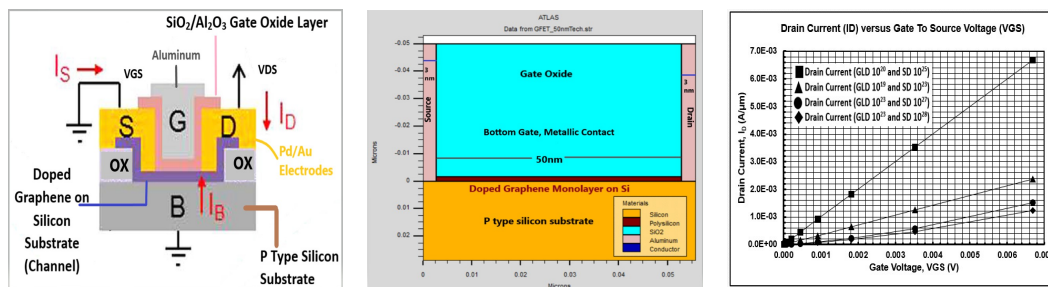


Figure01: (left) Theoretical structure of proposed device² (middle) simulated device (right) IV characteristics of the device at VDS = 0.2V

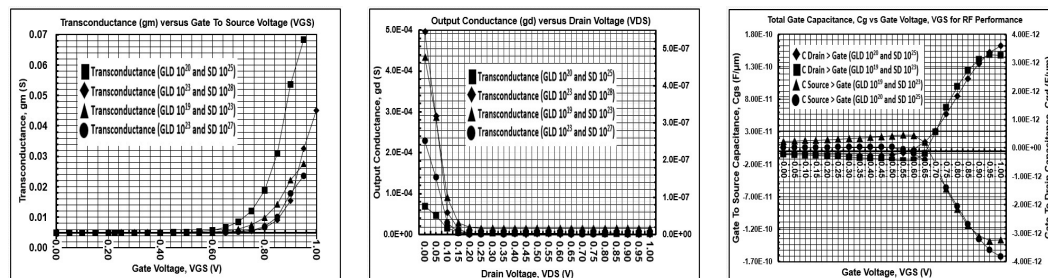


Figure 02: Transconductance vs gate voltage, Output conductance vs drain voltage and gate capacitance of the proposed device. Successful results verify the validity of the proposed device design.

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Sub-Sharvin conductance and enhanced shot noise in doped graphene

Ideal Sharvin contact in a multimode regime shows the conductance $G \approx G_{\text{Sharvin}} = g_0 k_F W / \pi$ (with g_0 the conductance quantum, k_F the Fermi momentum, and W the contact width) accompanied by strongly suppressed shot-noise quantified by small Fano factor $F \approx 0$. For ballistic graphene away from the charge-neutrality point the sub-Sharvin transport occurs, characterised by suppressed conductance $G \approx (\pi/4)G_{\text{Sharvin}}$ and enhanced shot noise $F \approx 1/8$. All these results can be derived from a basic model of quantum scattering, involving assumptions of infinite height and perfectly rectangular shape of the potential barrier in the sample. Here we have carried out the numerical analysis of the scattering on a family of smooth barriers of finite height interpolating between parabolic and rectangular shapes. We find that tuning the barrier shape one can modify the asymmetry between electron- and hole-doped systems. For electronic dopings, the system crosses from Sharvin to sub-Sharvin transport regime (indicated by both the conductance and the Fano factor) as the potential becomes closer to the rectangular shape. For hole dopings, the conductivity is strongly suppressed when the barrier is parabolic and slowly converges to $G \approx (\pi/4)G_{\text{Sharvin}}$ as the potential evolves towards rectangular shape. In such a case the Sharvin transport regime is inaccessible, shot noise is generically enhanced comparing to the electron-doped case, and aperiodic oscillations of both G and F are prominent due to the formation of quasibound states.

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Graphene nanodrums as valleytronic devices

We investigate the electronic transport in graphene nanoelectromechanical resonators (GrNEMS), known also as graphene nanodrums or nanomembranes. We demonstrate that these devices, despite small values of out-of-plane strain, between 0.1 and 1%, can be used as efficient and robust valley polarizers and filters. Their working principle is based on the pseudomagnetic field generated by the strain of the graphene membrane. They work for ballistic electron beams as well as for strongly dispersed ones and can be also used as electron beam collimators due to the focusing effect of the pseudomagnetic field. We show additionally that the current flow can be estimated by semiclassical trajectories which represent a computationally efficient tool for predicting the functionality of the devices.

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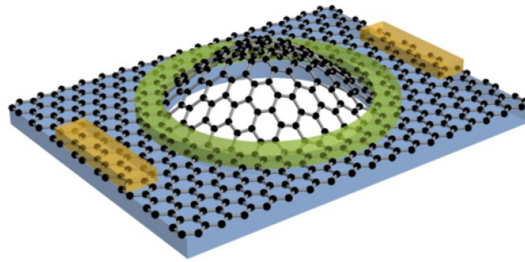


Figure 1: A graphene membrane deposited on an insulating substrate with a circular cavity forming a nanodrum. Current is injected and detected at the edges of the system.

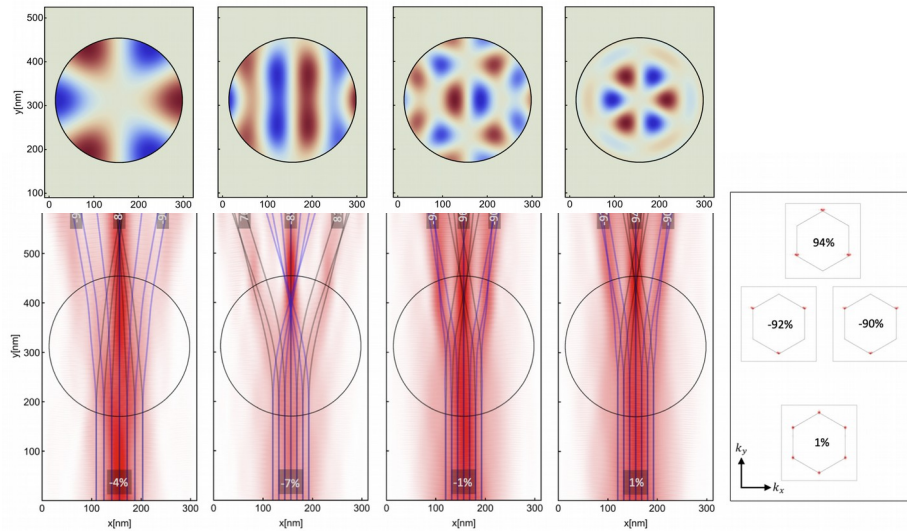


Figure 2: Nanodrum modes with pseudomagnetic field generated by the strain (top). Current flow split into three beams due to the pseudomagnetic field (bottom). Black and blue solid lines are semi-classical trajectories. The valley polarisations are measured in the Fourier space (right).

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Theory of the effective Seebeck coefficient for photoexcited graphene

Thermoelectric phenomena in photoexcited graphene have been the topic of several theoretical and experimental studies because of their potential usefulness in optoelectronic applications [1,2]. However, available theoretical descriptions of the thermoelectric effect in terms of the Seebeck coefficient do not take into account the role of the photoexcited electron density. In this work, [3] we adopt the concept of effective Seebeck coefficient [4] and extend it to the case of a photoexcited two-dimensional (2D) electron gas. We calculate the effective Seebeck coefficient for photoexcited graphene, we compare it to the commonly used “phenomenological” Seebeck coefficient, and we show how it depends on the photoexcited electron density and temperature. Our results are necessary inputs for any quantitative microscopic theory of thermoelectric effects in graphene and related 2D materials.

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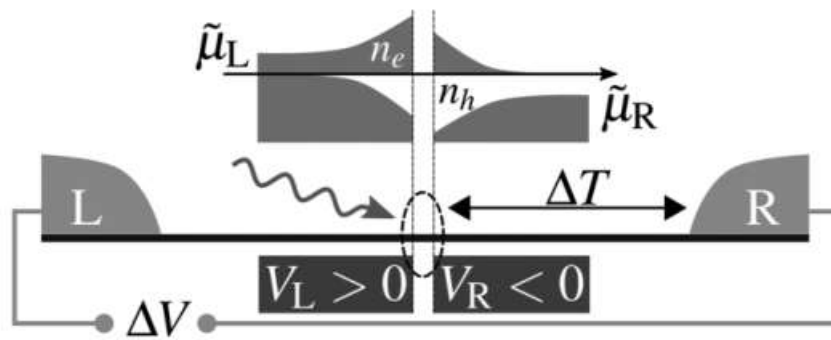


Figure 1: Radiation impinging onto a p-n junction (dashed oval) in graphene (thick line) induced by a split-gate (dark rectangles) with opposite potentials $V_{L,R}$. The electron (n_e , gray) and hole (n_h , white) densities in space are shown above graphene. The electrochemical potential ($\tilde{\mu}_{L,R}$) is well-defined away from the junction only, preventing the application of the standard expression for the thermoelectric current ($I=RS\Delta T$) between the contacts and the junction. The voltage ΔV is measured between the contacts L, R (light gray).

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Electron emission theory via tunneling in forward biased Graphene/n-GaAs Schottky Junctions

We propose new first-principles modeling for direct electron tunneling current in graphene/n-Semiconductor Schottky Barrier (SB) junction. Specifically, we consider a forward biased (FB) G/n-GaAs and develop a model of electronic tunneling and escape from graphene to the semiconductor. We model the tunneling process using a triangular barrier representing the FB junction. The junction barrier of height $q\phi_B$ represents the Schottky junction between graphene and semimetal where the quasi-Fermi levels split by an amount equal to the applied voltage. Typically, excited carriers in the graphene side may escape thermionically over the junction barrier or may tunnel through the junction barrier quantum mechanically. There are therefore two channels of carrier transport through the Schottky junction (a) thermionic escape (TE) to the other side and (b) thermionic field emission (TFE) through the barrier. In this communication we develop a detailed TFE tunneling diode model for net electron transport through the junction in both conduction directions (from the graphene to the semimetal side and vice versa). The graphene/n-GaAs system operates as a Schottky tunneling diode with current J_{TU} that includes several parameters of fundamental importance such as (a) new Richardson's constant A^* (b) WKB based transmission tunneling coefficient $T(E_z)$ (c) applied forward voltage and (d) a numerical factor dependent on diode parameters (n-type doping of the GaAs layer, effective electronic mass, built-in potential. The finalized current is an analytical result as: $J_{TU} = A^* I(T(E_z)) T^2 I(\lambda) \exp(-(q\Phi_B - E_{FL})/kT) \exp([\exp(V_a/V_t)-1])$ or expressed as a typical tunnel diode current density: $J_{TU} = J_{00} T^2 \exp(-(q\Phi_B - E_{FL})/kT) \exp([\exp(V_a/V_t)-1])$. We predict tunneling currents of 16.703 mA/cm² at 300°K, graphene/GaAs barrier height at 550meV, $A^* = 8.026A/cm^2 \text{ } ^\circ K^2$, V_a in a range from 0.2V to 1.2 V.

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Single Crystal, Large-area, Fold-free Monolayer Graphene

Chemical vapor deposition of carbon-containing precursors on metal substrates is currently the most promising route for the scalable synthesis of large-area high-quality graphene films. However, there are usually some imperfections present in the resulting films: grain boundaries, adlayers and wrinkle/folds, all of which can degrade the performance of graphene in applications.^[1] Numerous studies have been made on ways to eliminate grain boundaries and adlayers, but graphene folds have been less investigated. Here we explore the wrinkling/folding process for graphene films grown from an ethylene precursor on single-crystal Cu-Ni(111) foils.^[2] We identify a critical growth temperature (1030 K) above which folds will naturally form during the subsequent cooling process. Specifically, the compressive stress that builds up due to thermal contraction during cooling is released by the abrupt onset of step bunching in the foil at ~ 1030 K, triggering the formation of graphene folds perpendicular to the step edge direction. The resulting films show highly uniform transport properties: field-effect transistors prepared from these films exhibit average room temperature carrier mobilities of around $7.0 \pm 1.0 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for both holes and electrons. The process is also scalable, permitting simultaneous growth of graphene of the same quality on multiple foils stacked in parallel. After electrochemical transfer of the graphene films from the foils, the foils themselves can be reused essentially indefinitely for further graphene growth. *We appreciate support from the Institute for Basic Science (IBS-R019-D1).*

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Figures

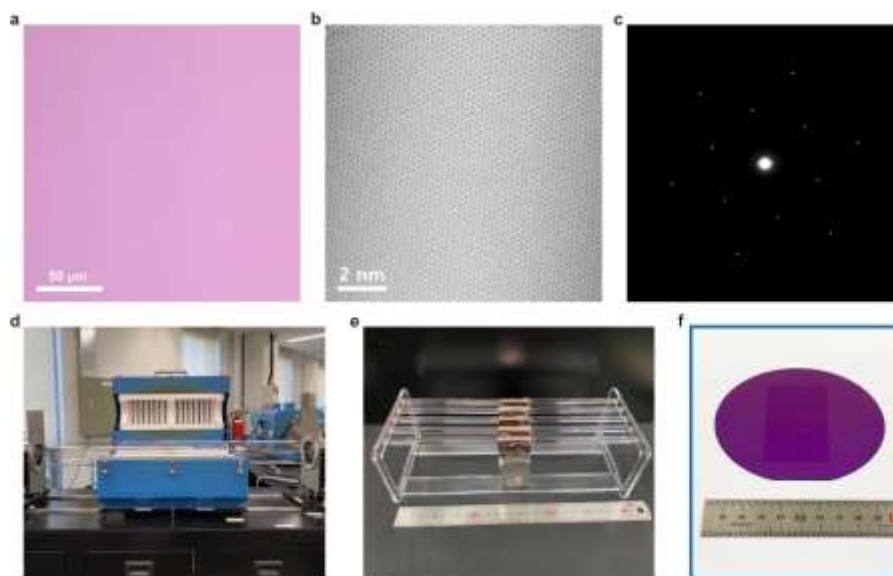


Figure 1: (a-c) Characterizations of fold-free single crystal single layer graphene films grown on Cu-Ni(111) foils with 20 at.% Ni. (d-f) Photos of scalable production of single-crystal fold-free graphene films.

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Phonon anharmonicity in supported single- and multi-layered WS₂ nanosheets – first principles and Raman investigation

The purpose of this work is the analysis of phonon anharmonicity in single- and multi-layered 2H-WS₂ nanosheets – a representative example among widely studied 2D transition metal dichalcogenides [1]. Anharmonicity has a significant impact on the temperature-dependent phonon properties: energies and lifetimes. For the supported samples, the substrate can further affect their vibrational properties. Although individual Raman studies with respect to temperature [2] and impact of the substrate – strain and charge doping [3] – are available for the most popular 2D materials (e.g., MoS₂), also for multi-layered nanosheets, a comprehensive ab-initio study of supported films with different numbers of layers is missing in the literature. Here, we present DFT simulations of temperature-dependent (0–500 K) phonon properties in 1–5 layered WS₂ nanosheets, including three-phonon interaction processes, thermal expansion, and substrate effects. We compare the simulated frequencies and bandwidths of the representative zone-center A_{1g} and E_{2g}¹ phonon modes to Raman spectra (75–500 K) measured in CVD-grown WS₂ thin films. We obtain a good agreement between ab-initio and experimental temperature trends (with respect to temperature-independent additive constants) in the case of A_{1g} (Figure 1) and high-temperature E_{2g}¹ phonons, whereas the low-temperature discrepancies for the E_{2g}¹ mode can be explained in terms of vertical strain distribution in multi-layered WS₂. Moreover, we simulate frequency shifts caused by interaction with the substrate, including mixed effects of charge doping and induced strain. The presented study of phonon anharmonicity is important due to its significant impact on thermal and electrical transport in nanosheets, including their potential applications. The results are also helpful for Raman characterization of supported WS₂ thin films at different temperatures.

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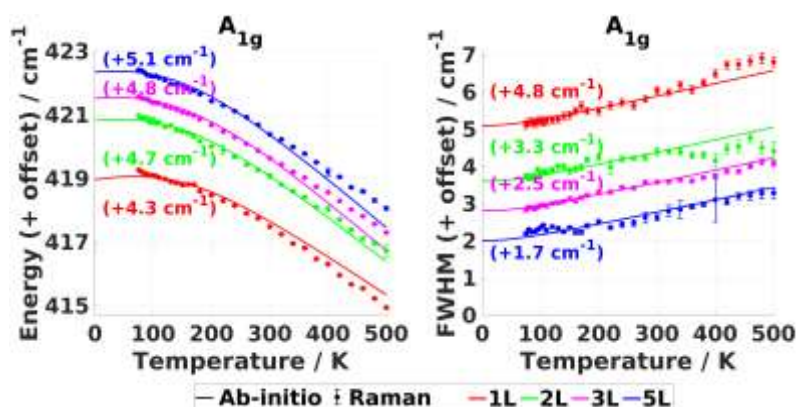
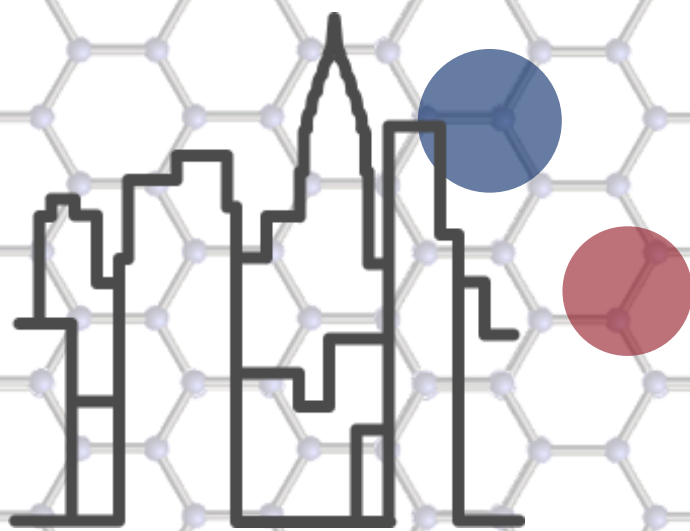


Figure 1: Temperature-dependent ab-initio and Raman results of energy and bandwidth of zone-center A_{1g} phonon mode in 1–5 layered WS₂ films. For clarity, the simulation results are shifted by additive constants (shown in brackets).



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Degradation of reduced graphene oxide in gastrointestinal fluids during *in vitro* digestion

Graphene nanomaterials (GFNs), including reduced graphene oxide (rGO), have distinctive characteristics that justifies the increased interest for them in the last years. They are being increasingly used in different fields, so it is important to evaluate its potential risk on human health.

According to the recommendation of the European Food Safety Authority (EFSA) and its guidance on risk assessment of nanomaterials to be applied in the food and feed chain: human and animal health¹, it is required to assess nanomaterial toxicity if exposure is evidenced. Thus, to check the stability of rGO (Graphitene, Ltd) on the gastrointestinal system we aimed to determine its *in vitro* digestion. This was carried using the method described by Diez-Quijada et al., 2020². Different synthetic juices that simulate the human digestive compartments (mouth, stomach, intestine, and colon), were used with 3 different rGO concentrations (200, 100, 50 µg/mL). rGO morphology was analyzed by scanning electron microscope (SEM). The surface charge and aggregation state were measured by ζ potential.

SEM images and ζ potential values showed the agglomeration of rGO samples as they pass through the different phases.

Thus, changes observed on the material can have an influence on its toxicity, aspect that should be further evaluated.

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A novel Zwitterionic Graphene oxide/Poly(vinylimidazole) material as an adsorbent for the removal of gold ions from aqueous solutions and a catalytic for the A₃ coupling

In this study, we have designed a novel multi-functional zwitterionic GO-based adsorbent for high-efficiency removal of AuCl_4^- ions from aqueous solutions and displaying a catalytic activity for the A₃ coupling. First, the functionalization of graphene oxide (GO) sheets by allylamine (Ally) was followed by in-situ polymerization of vinylimidazole (Vim) onto the GO-Ally surface. Then, the zwitterionic [GO-Ally-PolyVim-PS] material was obtained by grafting of 1,3-propanesultone (PS) onto the GO-Ally-PolyVim surface. The characterization of the zwitterionic GO-based material was investigated by Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA). Then, the adsorption behavior of zwitterionic [GO-Ally-PolyVim-PS] towards AuCl_4^- ions was studied as a function of the pH value and the contact time. In addition, to examine the mechanism of the adsorption process, pseudo-first, pseudo-second-order and intraparticle diffusion models were fitted to experimental kinetic data. It was shown that the pseudo-second-order model was appropriated to describe the AuCl_4^- ions and the spontaneous reduction of AuCl_4^- ions on the surface of zwitterionic [GO-Ally-PolyVim-PS] allowed the formation of gold nanoparticles (AuNPs). In addition, we studied the activity of [GO-Ally-PolyVim-PS]@AuNPs supported as a catalyst for the A₃ coupling of aldehydes, amines, and alkynes through C-H activation under green experimental conditions. Importantly, the heterogeneous catalyst [GO-Ally-PolyVim-PS]@AuNPs was consecutively recycled ten times without any loss of its activity.

Keywords: Graphene oxide sheets; Polymerization; Removal of AuCl_4^- ions; Catalytic activity; A₃ coupling

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Fizeau Drag In Graphene Plasmonics

Dragging of light by moving media was predicted by Fresnel and verified by Fizeau's celebrated experiments with flowing water. This momentous discovery is among the experimental cornerstones of Einstein's special relativity theory and is well understood in the context of relativistic kinematics. By contrast, experiments on dragging photons by an electron flow in solids are riddled with inconsistencies and have so far eluded agreement with the theory. Here we report on the electron flow dragging surface plasmon polaritons (SPPs): hybrid quasiparticles of infrared photons and electrons in graphene. The drag is visualized directly through infrared nano-imaging of propagating plasmonic waves in the presence of a high-density current. The polaritons in graphene shorten their wavelength when propagating against the drifting carriers. Unlike the Fizeau effect for light, the SPP drag by electrical currents defies explanation by simple kinematics and is linked to the nonlinear electrodynamics of Dirac electrons in graphene. The observed plasmonic Fizeau drag enables breaking of time-reversal symmetry and reciprocity at infrared frequencies without resorting to magnetic fields or chiral optical pumping. The Fizeau drag also provides a tool with which to study interactions and nonequilibrium effects in electron liquids.

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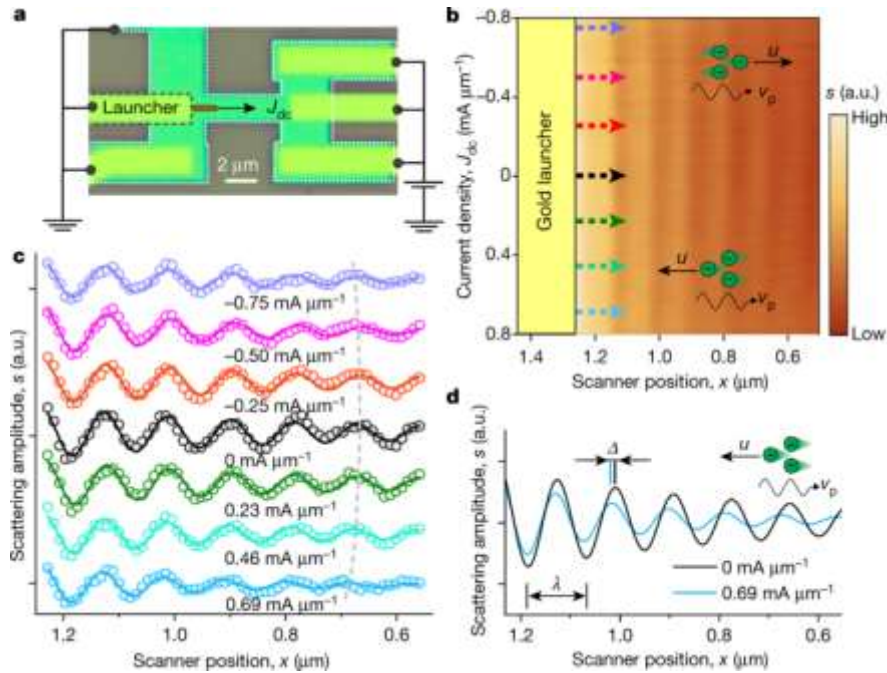


Figure 1: **a**, An optical image of a representative device. **b**, Near-field image, at $V_g = 47$ V and $T = 170$ K, acquired by scanning along the same line while varying the current density between ± 0.8 mA/μm. **c**, Averaged (± 25 μA/μm) SPP line profiles at different current densities. The circles are raw data; the solid lines are fitting results. The line profiles are shifted vertically for clarity. **d**, Fitted SPP line profiles without d.c. current (black) and with $J_{dc} = 0.69$ mA/μm (blue), illustrating a reduction of the SPP wavelength.

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Raman-based Quantitative Point Defect Density Comparison in Graphenic System

Since the isolation of the graphene from its bulk form in 2004, not only monolayer graphene but also few-layered forms, thus graphenic materials have been considered for a wide variety of applications. At the initial stage, all graphenes are extracted from bulk graphite via a mechanical exfoliation process. After a while, a chemical vapor deposition (CVD) route has been found and then large and continuous mono-to-few layer graphene has been available in recent years. Since a large number of defects in the CVD-based graphenic materials, sensitively changes the physico-chemical properties, thus the defect density must be carefully evaluated. Since most of the defect is point defect including vacancy, dopant, and topological defects, an imaging technique with sufficient atomic resolution needs to be used to identify these defects. Establishing experimental calibration, Cançado et al, proposed an equation that connects the Raman feature with ion irradiation created defect density in monolayer graphene [1]. Although exhaustive efforts have been devoted to understanding the correlation between Raman feature and defect density and layer count, a unified solution for the defect density evaluation in graphenic materials has not yet been proposed. In this context, here we propose a generalized way to quantitatively estimate the defect density in graphenic material via a non-destructive and non-contact Raman spectroscopy-based method. In this study, boron atoms substituting carbon atoms in the lattice of graphenic materials worked as point defects, and extracted boron-doped mono-to-few layered graphene has been subjected to the Raman spectroscopy investigation. Following the previous report [2], the substitutional boron atoms were introduced into bulk graphite flake using thermal diffusion of a boron atom, prior to mechanical exfoliation to obtain mono-to-few-layered graphenic materials. Detailed Raman spectroscopic analysis and collected more than 10k spectra revealed that data collected from graphenic materials that possess the same defect density form a line on the plane of A_{2D}/A_G – A_{2D}/A_G (Fig.1). Finally, a generalized equation to calculate defect density or average inter-defect distance was proposed.

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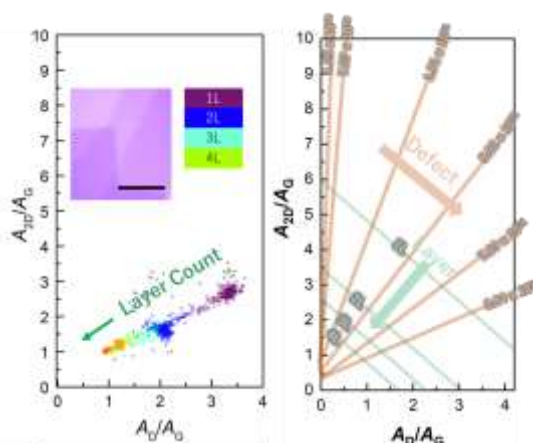


Figure 1: Raman data plotted on A_{2D}/A_G – A_{2D}/A_G plane.

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Ironing the 2D black phosphorus using electron beam irradiation

Layered nanomaterials are prone to formation of surface corrugations (wrinkles and ripples) and 2D nanomaterials like Black Phosphorous (BP) are extraordinarily affected by formation of such corrugations due to their high surface reactivity. The surface corrugations give rise to interface disorders such as interface coulomb contaminations, charge traps and local fluctuations in strain, polarised carrier puddles, dielectric screening and suppression of electron transport. While techniques like plasma treatment and thermal annealing have been reported in literature for removal of surface corrugations, the issue is far from resolved [1,2]. Here, we introduce an approach that utilizes electron beam of transmission electron microscope (TEM) for ironing out the wrinkles and ripples of BP flake (Figure 1a-b). Experimental results show the evolution of lattice ridden with line defects and declinations into the uniformly spaced parallel lattice planes which indicates the improvement in crystallinity of the flake under e-beam irradiation (figure 1 c-g). Prolonged exposure to e-beam causes buckling of flake and thus control over electron fluence rates or the exposure time is crucial for optimization of ironing process. The hitherto unattempted electron beam based ironing of 2D flakes with nanoscale precision is likely to open up new prospects for development of 2D nanomaterials with reproducible electron transport properties.

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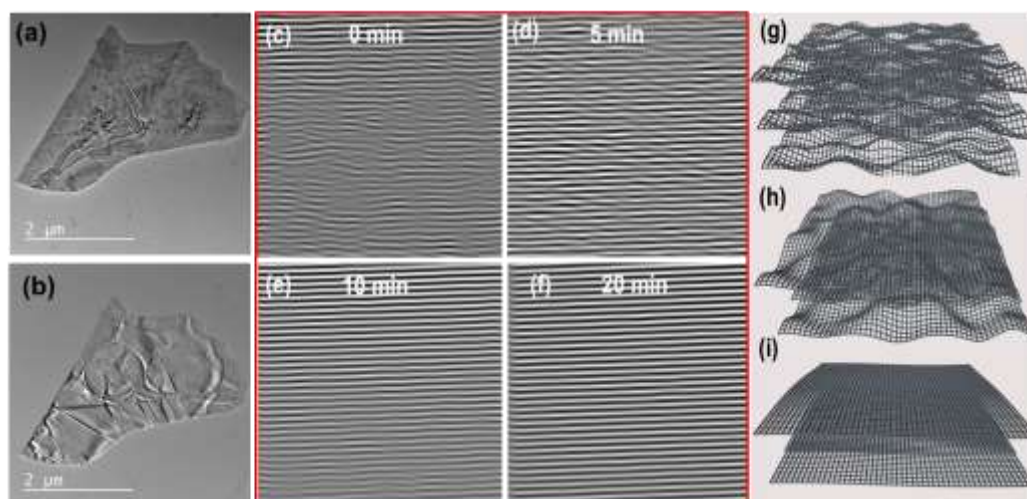


Figure 1: Low magnification TEM micrographs of BP flake (a) before and (b) after ironing. (c-f) Evolution of lattice fringes of BP with time under continuous exposure to electron beam in FEG-TEM set-up. (g-i) Schematic depicting the effect of electron beam irradiation on BP layers.

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Tuning van der Waals heterostructures by pressure

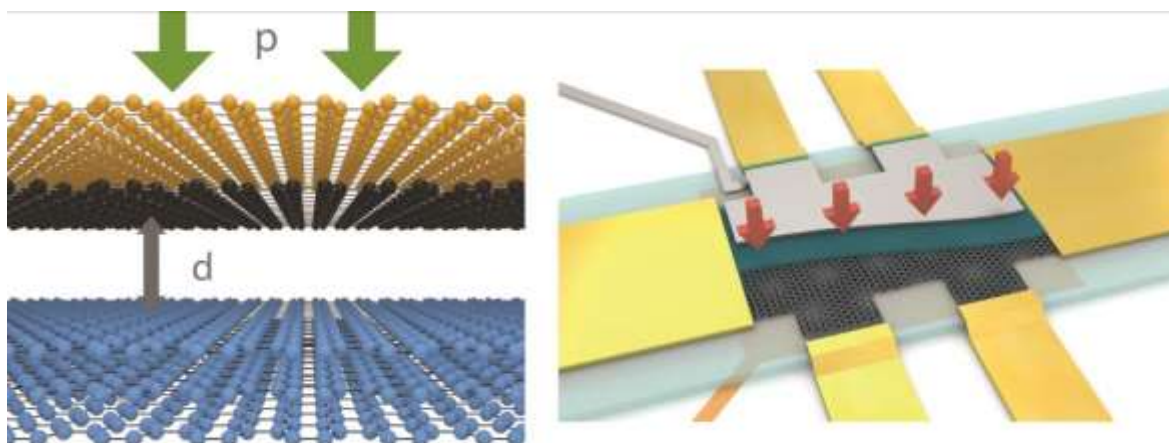
In van der Waals heterostructures the layer distance strongly affects the interaction between the layers. Therefore, pressure is an ideal tool to engineer the band structure of van der Waal materials [1].

In this talk I will show two examples for the versatility of this method. First, I will show, that in WSe₂/Gr structures spin-orbit coupling can be induced in graphene using proximity effects, which can be boosted using hydrostatic pressure [2]. The enhancement is confirmed using weak anti-localization measurements. Moreover, I will also demonstrate the band structure tuning of magic-angle twisted double bilayer graphene [3]. We have performed thermal activation and magneto-transport measurements to reveal changes in the bandgaps of the system. We have observed a strong tuneability with pressure, which is confirmed by our theoretical calculations. Finally, we have also observed changes in the strength of electron-electron interactions and in the topological phases at the charge neutrality point in magnetic fields.

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Figures



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Optoelectronic flexible devices based on WS₂ exfoliated by lithium intercalation

Alternative sources of energy have become crucial in the current environmental crisis. For example, converting strain, a temperature difference, or light into electrical current in materials supported on flexible substrates manages to reduce CO₂ emissions compared to traditional optoelectronic materials [1-3]. Moreover, when those materials, that exhibit optoelectronic characteristics, are low dimensional, the response increases considerably in contrast with their bulk counterpart [2]. For example, when transition metal dichalcogenides (TMDs) are exfoliated to obtain monolayers, their bandgap changes from an indirect transition to a direct one, thus enhancing the photocurrent [4]. The purpose of our study is to develop and measure optoelectronic flexible devices based on tungsten disulfide (WS₂). This is done by exfoliating WS₂ via lithium intercalation and then printing WS₂ on paper. The fabrication of optoelectronic devices was achieved, managing to reach sensibilities of over 10% of dark conductivity and responsivities over 20 μ AW⁻¹. This research will lead to the production of efficient optoelectronic flexible devices based on TMDs.

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Figures



Figure 1: Photocurrent measurement set-up and WS₂ based device printed on paper.

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Quantum Point Contacts in Monolayer WSe₂

Abstract

Quantum point contacts (QPCs) have been realized in III-IV semiconductor heterostructures, and more recently in bilayer graphene and trilayer WSe₂ [1, 2]. These QPCs are fabricated in these two-dimensional systems using electrostatic gates, and require ballistic transport from source to drain contact to observe conductance quantization. In this work, we show that it is possible to achieve high-quality QPCs on monolayer WSe₂ due to improvements in materials synthesis and contact quality. Measurements down to millikelvin temperatures show clear conductance quantization over micron-sized source-drain length scales. In WSe₂, at zero field, a two-fold degeneracy is expected at the top of the valence band due to the presence of strong spin-orbit interactions. Surprisingly, we find that the observed conductance plateaus are quantized in units of e^2/h , indicating that the spin-valley degeneracy is lifted even without the application of magnetic fields. Further, the first plateau has a systematic dependence on charge carrier density and on applied magnetic field, in a manner similar to the "0.7-anomaly" reported in previous experiments on III-V semiconductors [3]. We will discuss the nature of the anomaly seen here and the relevance of spin-orbit coupling to transport through this system.

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Figures

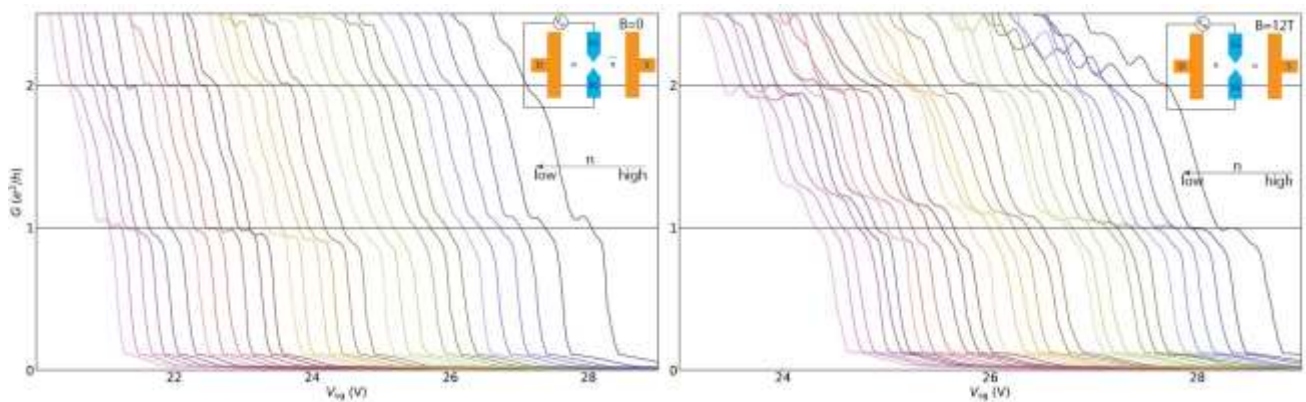


Figure 1: Conductance as a function of the split-gate voltage at zero magnetic field (left) and $B=12\text{ T}$ (right). The rightmost (leftmost) curves correspond to the highest (lowest) carrier density outside the QPC channel. Measurements are performed at 10mK.

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