



BOOK OF ABSTRACTS

International conference on Novel 2D materials explored via scanning probe microscopy & spectroscopy

June 25th - 29th, 2018 Donostia / San Sebastián - Basque Country, Spain

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Aim and Scope

Since its abrupt emergence in 2004, 2D materials have concentrated the research efforts of a large portion of the scientific community. Those novel materials combine tantalizing fundamental properties with the most promising applications. In 2D materials, essentially everything takes place on the surface and, consequently, SPM techniques have produced some of the most exciting works in these unique materials. This focused 2DSPM international conference will bring together a good number of the leading researchers on the field. The aim is to provide a very stimulating environment facilitating the easy flow of knowledge and ideas between participants.

Organizers:

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Scientific program

Monday, June 25th

09:00 - 09:15	REGISTRATION	
09:15 - 10:00	Steven G. Louie	Topological and interaction effects in atomically thin 1D and 2D materials
10:00 - 10:45	Michael F. Crommie	Imaging the quantum spin Hall effect in the 1T' phase of single-layer TMD materials
10:45 - 11:15	COFFEE BREAK	
11:15 - 12:00	Nacho Pascual	Inducing magnetism in graphene nanoribbons on surfaces
12:00 - 12:20	Roberto Otero	Relativistic dispersion of massive electrons in graphene nanoribbons
12:20 - 12:40	Aitor Mugarza	Hierarchical synthesis of nanoporous graphene with novel 1D electronic states
12:40 - 13:00	Aran García-Lekue	Atomistic insights into the chemical tuning of graphene nanoribbons
	LUNCH	
13:00 - 15:00		LUNCH
13:00 – 15:00 15:00 – 15:45	Jean-Yves Veuillen	LUNCH STM characterization of graphene-2D semiconductor heterostructures
13:00 - 15:00 15:00 - 15:45 15:45 - 16:05	Jean-Yves Veuillen Hervé Courtois	LUNCH STM characterization of graphene-2D semiconductor heterostructures Graphene response to charge disorder on the local scale
13:00 - 15:00 15:00 - 15:45 15:45 - 16:05 16:05 - 16:25	Jean-Yves Veuillen Hervé Courtois Thilo Glatzel	LUNCH STM characterization of graphene-2D semiconductor heterostructures Graphene response to charge disorder on the local scale Decoupling of graphene by KBr intercalation on Cu(111)
13:00 - 15:00 $15:00 - 15:45$ $15:45 - 16:05$ $16:05 - 16:25$ $16:25 - 16:45$	Jean-Yves Veuillen Hervé Courtois Thilo Glatzel Cristina Africh	LUNCH STM characterization of graphene-2D semiconductor heterostructures Graphene response to charge disorder on the local scale Decoupling of graphene by KBr intercalation on Cu(111) Real-time imaging of adatom-promoted graphene growth on nickel
13:00 - 15:00 $15:00 - 15:45$ $15:45 - 16:05$ $16:05 - 16:25$ $16:25 - 16:45$ $16:45 - 17:15$	Jean-Yves Veuillen Hervé Courtois Thilo Glatzel Cristina Africh	LUNCH STM characterization of graphene-2D semiconductor heterostructures Graphene response to charge disorder on the local scale Decoupling of graphene by KBr intercalation on Cu(111) Real-time imaging of adatom-promoted graphene growth on nickel COFFEE BREAK
13:00 - 15:00 $15:00 - 15:45$ $15:45 - 16:05$ $16:05 - 16:25$ $16:25 - 16:45$ $16:45 - 17:15$ $17:15 - 18:00$	Jean-Yves Veuillen Hervé Courtois Thilo Glatzel Cristina Africh Joaquín Fernández- Rossier	LUNCH STM characterization of graphene-2D semiconductor heterostructures Graphene response to charge disorder on the local scale Decoupling of graphene by KBr intercalation on Cu(111) Real-time imaging of adatom-promoted graphene growth on nickel COFFEE BREAK Probing magnetism in 2D van der Waals crystalline insulators via electron tunneling

Tuesday, June 26th

09:15 - 10:00	Ali Yazdani	Visualizing quantum Hall liquids and their topological boundary modes
10:00 - 10:45	Peter Wahl	Atomic scale imaging of strain-tuned emergent phases of matter
10:45 - 11:15	COFFEE BREAK	
11:15 – 12:00	Roland Wiesendanger	Interfacial superconductivity in 2D layers of Fe- chalcogenides on topological insulators studied by Spin-Resolved Scanning Tunneling Spectroscopy
12:00 - 12:20	Carmen Rubio- Verdú	Multifractal superconductivity in single-layer NbSe ₂
12:20 - 12:40	Liguo Ma	Visualizing the electronic structure of atomically thin High-Tc crystals
12:40 - 13:00	Deung-Jang Choi	Probing magnetic interactions between Cr adatoms on the Bi ₂ Pd superconductor
13:00 - 15:00	LUNCH	
15:00 - 15:45	Rubén Pérez	Novel theoretical approaches to extract information from STM and AFM experiments in 2D materials
15:45 - 16:05	Andrea Droghetti	Tailoring charge and spin transport in molecule/layered material interfaces
16:05 - 16:25	Bruno de la Torre	Non-covalent control of spin-state in metal-organic complex by positioning on n-doped graphene and its SPM discrimination
16:25 - 16:45	Jérome Lagoute	Electronic interaction between organic molecules
		ana grupnene
16:45 – 17:15		COFFEE BREAK

Wednesday, June 27th

09:15 - 10:00	Markus Morgenstern	<i>Giant tuning of graphene's pseudospin polarization</i> <i>and valley splitting by a scanning tunneling</i> <i>microscope</i>
10:00 - 10:45	Abhay Pasupathy	Tunable strain solitons in transition metal dichalcogenides
10:45 - 11:15	COFFEE BREAK	
11:15 - 12:00	Joseph A. Stroscio	Visualizing the interplay between spatial and magnetic confinement in graphene quantum dots
12:00 - 12:20	Eva Cortés-Del Río	Quantum confinement of graphene massless Dirac quasiparticles
12:20 - 12:40	Julia Tesch	Landau quantization in graphene/transition metal dichalcogenides probed at the local scale
12:40 - 13:00	Soon Jung Jung	Electric field effect on the intramolecular hydrogen transfer of phthalocyanine molecule
13:00 - 15:00	LUNCH	
15:00 - 15:45	Philip Hofmann	Electronic structure and electron dynamics in two- dimensional Dirac materials
15:45 - 16:05	Felix Flicker	Charge order in NbSe ₂
16:05 - 16:25	Arpad Pásztor	Non-monotonic thickness dependence of the charge density wave order parameter in VSe ₂
16:25 – 16:45	Ion Errea	CDW temperature in bulk and monolayer transition metal dichalcogenides from first-principles
16:45 – 17:15	COFFEE BREAK	
17:15 - 18:00	Tim Wehling	Electronic correlations and competing interactions in two-dimensional materials
18:00 - 18:20	Cesare Tresca	Chiral spin texture in the charge-density-wave phase of the correlated metallic Pb/Si(111) monolayer
20:45	CONFERENCE DINNER in "Ni neu" restaurant	

Thursday, June 28th

10:00 - 10:45	Chih-Ken Shih	Atomic and electronics structures of 2D electronic materials and their heterostructures
10:45 - 11:15	COFFEE BREAK	
11:15 – 12:00	Thomas Michely	Quantization effects and spin charge separation in metallic wires: mirror twin boundaries in monolayer MoS_2 on graphene
12:00 - 12:20	Sara Barja	Electronic properties of defects in single-layer MoSe ₂
12:20 - 12:40	Matthias Batzill	Grain boundary formation in MoTe ₂ by excess-Mo incorporation into the lattice
12:40 - 13:00	Vincent Renard	Twisted graphene layers under heterostrain
13:00 - 15:00	LUNCH	
15:00 - 15:45	Katarina Franke	Defects and molecular adsorbates on monolayers of MoS ₂ on Au(111)
15:45 – 16:05	Blanca Biel	Mind the substrate: SPM characterization of point-like defects in single-layer MoS ₂ on metallic substrates
16:05 - 16:25	Bruno Schuler	Exploring optoelectronic properties of point defects in monolayer WS ₂ with atomic resolution
16:25 - 16:45	Michele Pizzochero	Intrinsic and engineered point defects in two- dimensional 1T'-MoS ₂
16:45 – 17:15	COFFEE BREAK	
17:15 – 18:00	Oleg V. Yazyev	1D defects in 2D materials: a theorist's view
18:00 - 18:20	Luca Chirolli	Polariton Hall effect in transition-metal dichalcogenides

Friday, June 29th

09:15 - 10:00	Harald Brune	Realization of single atom magnets through 2D decoupling layers
10:00 - 10:45	Jürg Osterwalder	A closer look at electrochemically transferred 2D materials
10:45 - 11:15	COFFEE BREAK	
11:15 - 12:00	Michael S. Fuhrer	Atomically thin films of Na ₃ Bi: A platform for topological electronics
12:00 - 12:20	Jiong Lu	Probing electrical field tunable bandgap and defects in black phosphorus
12:20 - 12:40	Sara Mueller	Group IV analogs to graphene
12:40 - 13:00	Moon-Ho Jo	Electric field effect on the intramolecular hydrogen transfer of phthalocyanine molecule

Oral Contributions

Topological and Interaction Effects in Atomically Thin 1D and 2D Materials

Steven G. Louie¹

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We show that new topological characteristics can manifest in the electronic states of 1D and 2D systems owing to reduced dimensionality, giving rise to unconventional electronic and optical behaviors. Two distinctive findings will be presented in this talk. First, we have predicted that graphene nanoribbons (GNRs) of different width, edge, and end termination (synthesizable in experiments) belong to different electronic topological classes [1]. We derived explicit formulas for their topological invariants and showed that junction states between two GNRs of distinct topology may be tuned by lateral junction geometry. Superlattices of such states exhibit remarkable properties that are tunable (e.g., forming a robust antiferromagnetic spin chain or having new topological-derived bands of different size gap). Second, we have shown that the conventional optical selection rules for excitons must be replaced in 2D by a new simpler formula, owing to a topological characteristic inherent to the photoexcitation of excitons in 2D materials [2]. The new selection rule states that optically active exciton states in 2D must have an envelope-function angular quantum number equal to the winding number of the interband optical transition matrix elements (a heretofore unrecognized topological invariant). As illustration, this appealingly simple new rule is applied to elucidate the optical spectrum of three gapped graphene systems. Both theoretical predictions have been observed in experiments [3,4].

- [1] T. Cao, F.-Z. Zhao, and S. G. Louie, Phys. Rev. Lett. 119, 076401 (2017).
- [2] T. Cao, M. Wu, and S. G. Louie, Phys. Rev. Lett. 120, 087402 (2018).
- [3] L. Ju, L. Wang, T. Cao, T. Taniguchi, K. Watanabe, S. G. Louie, F. Rana, J.-W. Park, J. Hone, F. Wang, and P. L. McEuen, *Science* 358, 907 (2017).
- [4] D. J. Rizzo, G. Veber, T. Cao, C. Bronner, T. Chen, F.-Z. Zhao, H. Rodriguez, S. G. Louie, M. F. Crommie, F. R. Fischer, to be published.

Imaging the quantum spin Hall effect in the 1T' phase of single-layer TMD materials

M. F. Crommie^{1,2}

¹UC Berkeley Physics Department, Berkeley, CA, US ²Materials Sciences Division, LBNL, Berkeley, CA, US

The transition metal dichalcogenides (TMDs) exhibit a variety of behavior due to their strong spin-orbit coupling, electron-electron interactions, and electron-phonon coupling. Recently the quantum spin Hall effect (QSHE) was predicted to occur in the 1T' phase of TMD materials when they are thinned down to a single layer.¹ I will discuss our efforts to test this prediction in single layers of WTe₂ and WSe₂ grown via molecular beam epitaxy. Using angle-resolved photoemission (Stanford, LBNL ALS) and scanning tunneling microscopy/spectroscopy (UC Berkeley), we have observed evidence for the QSHE in the form of band inversion and edge-states. The variety of phases in this class of material creates new opportunities for exploring edge-state behavior at atomically-precise interfaces, including well-ordered 1T'-1H phase boundaries that exhibit topologically-protected states and 1T'-1T' boundaries that exhibit unprotected edge-states. We find that different phase boundaries in 2D QSHI materials can be induced by excitation from the tip of a scanning tunneling microscope.

References:

[1] X. Qian, J. Liu, L. Fu, and J. Li, "Quantum spin Hall effect in two-dimensional transition metal dichalcogenides", *Science* **346**, 1344 (2014).

Inducing magnetism in graphene nanoribbons on surfaces

Jingcheng Li¹, Nestor Merino^{1,2}, Martina Corso^{2,3}, Diego Peña⁴, Dimas G. De Oteyza^{2,3} and <u>Nacho Pascual^{1,2}</u>

¹CIC nanoGUNE, Donostia San Sebatián, Spain ²Donostia International Physics Center- DIPC, Donostia San Sebatián, Spain ³Centro de Física de Materiales CFM-CSIC/UPV-EHU ⁴CIQUS, Universidad de Santiago de Compostela, Spain

Large aromatic carbon nanostructures are cornerstone materials due to their increasingly role in functional devices. Among the many predicted applications, magnetism is the most unexpected one, but still an attractive challenge for its active role in spintronic devices. In our laboratories we aimed at exploring different methods for turning graphene nanoribbons (GNRs) magnetic using low temperature scanning tunneling microscopy (STM). The production of GNR can be realized with atomic precision on a metal surface using chemical strategies of on-surface synthesis [1], resulting in mostly defect-free ribbons and with a customized shape according to the utilized precursor.

The simplest method to induce magnetism is to induce defects [2] or to dope the carbon network with magnetic species. We will show that it is possible to incorporate magnetic molecular species into a ribbon using on-surface synthesis routes (see included image of a Fe porphyrin contacted to chiral nanoribbons). We prove that the molecular spin survives in the ribbon by using spin-excitation inelastic spectroscopy [3]. However, numerous predictions state that graphene can also spontaneously develop magnetism from the Coulomb repulsion of its pi-electrons. Crucial examples are the magnetization of zig-zag edges in graphene, or the emergence of paramagnetism in open shell



graphenoid nanostructures. We will show that graphene nanostructures indeed may exhibit fingerprints of piparamagnetism on a metal surface that can be detected and localized with STM.

- [1] J. Cai et al, Nature 466, 470 (2010).
- [2] H. Gonzalez-Herrero, et al., Science 352, 437 (2016).
- [3] J. Li, et al, Science Adv. 4, eaaq0582 (2018)

Relativistic Dispersion of Massive Electrons in Graphene Nanoribbons

R. Otero^{1,2}, B. Cirera², A. Martin-Jimenez², J. M. Gallego³, D. Écija², R. Miranda^{1,2}

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Quantum confinement of massless Dirac fermions in graphene nanoribbons (GNRs) leads to the opening of a gap and a non-zero effective mass of the charge carriers, an essential step for the integration of such materials as circuit elements. Previous determinations of the effective mass using experimental band dispersions have yielded surprisingly inconsistent results [1-3]. Here we show that the experimental dispersion relation of 6-aGNRs determined by Scanning Tunnelling Spectroscopy can be accurately described with a model that discretizes the full band dispersion of graphene. Our results demonstrate that the electrons in GNRs satisfy a hyperbolic relativistic dispersion relation for massive particles. A parabolic fit will therefore yield accurate values of the effective masses only for low electron momentum, so that the electron wavelength is much larger than the "Compton" wavelength of the relativistic electrons.

- [1] P. Ruffieux, J. M. Cai, N. C. Plumb, L. Patthey, D, Prezzi, A. Ferretti, E. Molinari, X. L. Feng, K. Mullen, C. A.Pignedoli, and R. Fasel, ACS Nano 6, 6930 (2012).
- [2] H. Söde, L. Talirz, O. Gröning, C. A. Pignedoli, R. Berger, X. Feng, K. Müllen, R. Fasel, and P. Ruffieux, Phys. Rev. B 91, 045429 (2015).
- [3] E. Carbonell-Sanromà, P. Brandimarte, R. Balog, M. Corso, S. Kawai, A. Garcia-Lekue, S. Saito, S. Yamaguchi, E. Meyer, D. Sanchez-Portal, and J. I. Pascual, Nano Lett. 17, 50 (2017).



Fig 1. (a) $4,3 \times 9,7$ nm² STM topographic image of 6-aGNR linked to two polyphenylene wires with the chemical scheme superimposed. (It = 50 pA, Vb = -500 mV,). (b) STS spectra taken at different positions indicated in (a). (c) Differential conductance maps recorded at the energies of the confined states. (d) Stack of STS spectra recorded along the long axis of the 6-aGNR box. (e) Line-by-line FFT of a) showing the dispersion relation, E vs k. Dotted white line: dispersion calculated with our discretization model. Full blue line: relativistic hyperbola (maximum group velocity v = 8.1×10^5 m/s; effective mass 0.12me). Dashed blue line: non-relativistic parabola (bottom of the band +0:43 eV; effective mass 0.19me). (f) Left panel: Conduction subbands for 6 aGNR. Vertical dotted lines correspond to the discrete values of the parallel momentum and the corresponding discrete energy levels are highlighted with square symbols. The correspondence between these calculated energy levels and the peaks of the experimental dI/dV curves (right panel) is shown by horizontal arrows.

Hierarchical synthesis of nanoporous graphene with novel 1D electronic states

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Nanosize pores can turn semimetallic graphene into a semiconductor (1, 2) and from being impermeable into the most efficient molecular sieve membrane (3, 4). However, scaling the pores down to the nanometer, while fulfilling the tight structural constraints imposed by applications, represents an enormous challenge for present top-down strategies.

Here we report a bottom-up method to synthesize nanoporous graphene comprising an ordered array of pores separated by ribbons, which can be tuned down to the one nanometer range (5). The size, density, morphology and chemical composition of the pores are defined with atomic precision by the design of the molecular precursors. Our DFT-STS study further reveal a highly anisotropic electronic structure, where orthogonal one-dimensional electronic bands with an energy gap of ~1 eV coexist with confined pore states that can be regarded as 2D analogues of the superatom states found in fullerene (6). The combined structural and electrical properties makes this nanoporous 2D material a highly versatile semiconductor for simultaneous sieving and electrical sensing of molecular species.

References:

- [1] J. Bai, X. Zhong, S. Jiang, Y. Huang, X. Duan, Graphene nanomesh. Nat. Nanotechnol. 5, 190–194 (2010)
- [2] X. Liang *et al.*, Formation of Bandgap and Subbands in Graphene Nanomeshes with Sub-10 nm Ribbon Width Fabricated via Nanoimprint Lithography. *Nano Lett.* **10**, 2454–2460 (2010)
- [3] S. Garaj et al., Graphene as a subnanometre trans-electrode membrane. Nature. 467, 190–193 (2010)
- [4] S. P. Koenig, L. Wang, J. Pellegrino, J. S. Bunch, Selective molecular sieving through porous graphene. *Nat. Nanotechnol.* 7, 728–732 (2012)
- [5] C. Moreno et al., Bottom up synthesis of multifunctional nanoporous graphene. Science, accepted
- [6] M. Feng, J. Zhao, H. Petek, Atomlike, hollow-core-bound molecular orbitals of C60. Science. 320, 359-62 (2008)



Fig 1. STM images (bottom) and schematic representation (top) of the precursor, intermediates and final product of the hierarchical synthesis of nanoporous graphene. The high resolution images of the nanoribbon and nanoporous graphene have been obtained with a CO-functionalized tip.

Atomistic Insights into the Chemical Tuning of Graphene Nanoribbons

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Chemical modification may serve as a powerful tool to enhance the optical, electronic and magnetic functionalities of graphene nanoribbons (GNRs). Thus, aimed at their use in real applications, an atomic level understanding and control of the GNR properties depending on the nature, location and periodicity of the dopants is desirable.

Using *ab initio* methods, and in close collaboration with our experimental colleagues, we have studied the electronic and transport properties of GNRs doped and functionalized in different ways. On one hand, we have investigated the properties of armchair GNRs doped with substitutional boron pairs in the central backbone, for two experimentally accessible cases: periodically B-doped ribbons, and ribbons with pristine segments separated by regions doped with B pairs. Besides, we have studied the influence of edge doping, using for this purpose chiral and chevron GNRs functionalized with amino and fluorine groups, respectively. Our findings are compared with scanning tunneling microscopy/spectroscopy (STM/STS) and angle-resolved photoemission (ARPES) data. Depending on the doping mechanism, various effects are observed and interpreted, such as electron confinement by dopants, enhanced substrate-GNR interaction, energy gap modification, or energy shifts of frontier orbitals. [1,2]

References:

- [1] E. Carbonell-Sanromá et al., Nano Letters 17, 50 (2017)
- [2] M. Panighel et al. (in preparation)



Figure: (Top right) Hybrid nanoribbon composed of a pristine armchair GNR segment separated by regions with B pairs. (Left) Energy-resolved projected density of states for a pristine GNR segment enclosed between two borylated sections. Quantized levels up to N = 5 are clearly observed. (Bottom right) Eigenchannel wave functions at the energies corresponding to the N = 2, 3, 4, and 5 quantum well levels.

STM characterization of Graphene- 2D Semiconductor heterostructures

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Van der Waals heterostructures [1] formed by vertically stacking two-dimensional (2D) materials have a strong potential for the development of original devices. Our aim was to characterize graphene-(semiconducting) transition metal dichalcogenides (TMDs) interfaces, which are essential constituents in these heterojunctions, by means of scanning tunneling microscopy and spectroscopy (STM/STS). Our samples were made of either MBE grown or mechanically transferred flakes deposited on epitaxial mono (MLG) or bilayer graphene (BLG) grown on SiC. In both cases, we find no evidence for Fermi level pinning at these 2D metal-semiconductor junctions [2], in agreement with theoretical predictions [3]. Most of the point defects appear to be neutral. However, we could identify some negatively charged defects from their strong electronic contrast. Spatially resolved STS maps give access to the band bending around charged defects (see Figure 1), which is of the order of a fraction of 1 eV, extending over a few nm's for the charged 0D and 1D defects we have analyzed [4]. Finally, we study (diffuse) lateral TMD heterojunctions prepared by MBE. They show the expected type II band alignment [5] without any evidence for interface states.

References:

- [1] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, Science 353, 6298 (2016)
- [2] T Le Quang, V Cherkez, K Nogajewski, M Potemski, M T Dau, M Jamet, P Mallet, J-Y Veuillen, 2D Mater. 4, 035019 (2017)
- [3] Liu Y, Stradins P and Wei S-H, Sci. Adv. 2 e1600069 (2016)
- [4] T Le Quang, V Cherkez, K Nogajewski, M Potemski, M T Dau, M Jamet, P Mallet, J-Y Veuillen, submitted to 2D Mater.



[5] S. Yoshida et al., Sci. Rep. 5, 14808 (2015)

Fig 1. Spectroscopy of a charged defect in an exfoliated 3L-WSe₂ sample. (a) Spectra taken close to the defect and on the bare surface highlighting the shift of the main structures at the defect site. Inset : image of the area taken at +1.25 V, scale bar is 2.8 nm. (b) Spatial variation of the band bending (mostly occurring in region II) around the defect in (a) obtained from the spatial variations of the spectroscopic structures.

Graphene response to charge disorder on the local scale

<u>Hervé Courtois</u>¹, Sayanti Samaddar¹, Sylvain C. Martin¹, Indra Yudhistira², Shaffique Adam², Johann Coraux¹, Benjamin Grévin³, and Clemens B. Winkelmann¹

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The charge carrier density in graphene on a dielectric substrate such as SiO_2 displays inhomogeneities, the so-called charge puddles. Because of the linear dispersion relation in monolayer graphene, the puddles are predicted to grow near charge neutrality, a markedly distinct property from conventional two-dimensional electron gases.

We combine *in situ* scanning tunneling microscopy/spectroscopy, Kelvin probe force microscopy and transport measurements on a single mesoscopic graphene device. This allows us to directly observe the puddles' growth, both in spatial extent and in amplitude, as the Fermi level approaches the Dirac point [1]. Self-consistent screening theory provides a unified description of both the macroscopic transport properties and the microscopically observed charge disorder.

We further show that local variations of the Fermi level with respect to the band structure are in one-toone correspondence with changes in the local work function, down to the nanometer scale [2].

References:

[1] S. Samaddar, I. Yudhistira, S. Adam, H. Courtois, and C. B. Winkelmann, Phys. Rev. Lett. **116**, 126804 (2016).

[2] S. Samaddar, J. Coraux, S. C. Martin, B. Grévin, H. Courtois, and C. B. Winkelmann, Nanoscale 18, 15162 (2016).



Fig 1. Top row: Left and center: 100 x 100 nm² maps of the local Dirac point energy in a single layer graphene on SiO_2 when the Fermi level is tuned from p-doping (left) to the Dirac point (center). Doping inhomogeneities (puddles) grow, both in lateral extent and in amplitude. Right: puddles size dependence on back-gate voltage. **Bottom row:** As the relative position of the Fermi level with respect to the band structure varies, as a function of position across a graphene wrinkle in graphene on Ir(111) (Left, AFM topography) or back-gate voltage in graphene on SiO_2 (Right, AFM phase image superimposed on topography), the work function varies accordingly.

Decoupling of graphene by KBr intercalation on Cu(111)

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The 2D material Graphene attracted wide attention owed to the remarkable optic and electronic properties. Defect free, monocrystalline graphene can be obtained by catalytic growth on transition metal surfaces. On the one hand this bottom-up approach provides a clean and controllable route. On the other hand, graphene's remarkable properties are reduced by the binding to the metal substrate. [1] By the intercalation of atoms and molecules graphene can be decoupled, restoring its electronic structure [2,3]. To the best of our knowledge no intercalation by ionic compounds has been reported. However, the decoupling of molecules by alkali halide thin films is a common method, utilized to study single molecules in scanning probe experiments.

We applied non-contact Atomic Force Microscopy (nc-AFM) to study the properties of graphene on clean Cu(111) and after the co-adsorption of KBr on Cu(111). By means of Kelvin probe force microscopy (KPFM) a change in graphene's work function has been observed after the deposition of KBr, indicating a restoration of the electronic properties of graphene. In addition, X-Ray photoelectron spectroscopy (XPS) showed a chemical shift in graphene's C1s core-level following the co-deposition. Further, a new chemical species for potassium has been observed in the presence of graphene. Angle dependent XPS measurements revealed that this new species was located underneath graphene, supporting intercalation as the decoupling mechanism. The results have been compared with density functional theory (DFT) calculations supporting our experiments findings.

References:

- [1] S. M. Kozlov, F. Viñes, A. Görling, J. Phys. Chem. C, 7360-7366 (2012)
- [2] L.Huang, Y. Pan, L. Pan, M. Gao, W. Xu, Appl. Phys. Lett. 99, 163107-1-3 (2011)
- [3] T. Bointon, I. Khrapach, R. Yakimova, Nano Lett. 15, 1751-1755 (2014)



Fig. 1: Change in the work-function of graphene upon KBr deposition. On bare copper the CPD of graphene (Gr_i) 850 mV (left), in presence of KBr the CPD of graphene (Gr_i) was 450 mV (right) in respect to copper.

Real-time imaging of adatom-promoted graphene growth on nickel

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Single adatoms are expected to participate in many processes occurring at the solid-gas and solid-liquid interfaces, including the growth of graphene on metal surfaces. However, a direct visualization at the atomic scale of such fast-evolving processes, essential to unveil their details, is typically hampered by the limited time resolution of commercial microscopes. By means of FAST, an add-on module developed in our laboratory [1], we were able to image the synthesis of graphene flakes on Ni(111) at technologically relevant temperatures (≈ 700 K), directly capturing the catalytic action of single metal adatoms at the graphene edge. Force-field molecular dynamics (MD) and ab-initio density functional theory (DFT) calculations rationalize the experimental observations, giving a complete description of the growth pathways. We show that single Ni atoms, diffusing on the metal surface, are temporarily trapped at kink sites along the graphene flake edges and facilitate the incorporation of new C atoms in the graphene network, which thus grows by ordered addition of couples of carbon rows parallel to the edge. Our results demonstrate that the combination of highspeed STM imaging and MD+DFT simulations provides essential details for a correct description at the atomic level of the synthesis of 2D materials [2].

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References:

[1] http://fastmodule.iom.cnr.it

[2] L. L. Patera et al., Science, 359, 1243-1246 (2018)



Fig 1. (A) Selected frames from an STM movie acquired during graphene growth at 710K (frame rate 60 Hz). (B) Ni adatoms diffusing on the Ni(111) surface towards the kinks at a graphene edge. A representative MD trajectory is shown. (C-L) Configurations of the Ni adatom at klein edge kinks: (C, G) High-speed STM images, (D, H) Laplace-filtered images with superimposed ball models, (E, I) DFT simulation of constant height STM images based on the calculated geometries in (F, L).

Probing magnetism in 2D van der Waals crystalline insulators via electron tunneling

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The recent discovery of 2D crystals that present magnetic order and can be integrated in Van Der Waals heterostructures is opening new ways to explore and manipulate low dimensional magnets. In this talk I will discuss how tunneling electrons can be used to probe magnetism of an atomically thin layers of CrI_3 , a layered insulating ferromagnetic compound. In particular, I will discuss our theoretical understanding of the very large magnetoresistance observed in magnetic tunnel junctions where a bilayer of CrI_3 is placed between two electrodes of graphite [1]. In addition, I will discuss how inelastic electron tunneling spectroscopy provides a very useful tool to probe magnons in this new class of materials [1]. Specifically, I will discuss how magnon renormalization, a phenomenon particularly strong for 2D magnetic systems, is revealed in the experiments, both with CrI_3 [1] and $CrBr_3$ [2].

- [1] Probing magnetism in 2D van der Waals crystalline insulators via electron tunneling. Dahlia R. Klein, David MacNeill, Jose L. Lado, David Soriano, Efrén Navarro-Moratalla, Kenji Watanabe, Takashi Taniguchi, Soham Manni, Paul Canfield, Joaquín Fernández-Rossier, Pablo Jarillo-Herrero. arXiv:1801.10075
- [2] Magnon-assisted tunneling in van der Waals heterostructures based on CrBr₃. Davit Ghazaryan, Mark T. Greenaway, Zihao Wang, Victor H. Guarochico-Moreira, Ivan J. Vera-Marun, Jun Yin, Yuanxun Liao, Serge V. Morozov, Oleg Kristanovski, Alexander I. Lichtenstein, Mikhail I. Katsnelson, Fred Withers, Artem Mishchenko, Laurence Eaves, Andre K. Geim, Kostya S. Novoselov, Abhishek Misra.

Probing the Interaction of Dirac Electrons with Spins and Point Charges

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Graphene in its pristine form has transformed our understanding of 2D electron systems leading to fundamental discoveries and to the promise of important applications. When graphene's perfect honeycomb lattice is disrupted by single atom vacancies new phenomena emerge that are driven by the interaction of graphene's Dirac electrons with the vacancy intrinsic charge and its intrinsic spin. I will describe scanning tunneling microscopy and spectroscopy measurements that probe these phenomena. i) By applying voltage pulses to the vacancy site, the initially uncharged vacancy is gradually charged into a regime where the Dirac electrons become trapped in quasi-bound states that resmble an artificial atom^{1,2,3}. ii) Identifying Kondo screening of the vacancy spin by its spectroscopic signature, we show that the local magnetic moment can be controlled either by doping or through graphene's local curvature. This allows to detect and map the quantum phase transition separating magnetic from non-magnetic states in this pseudogap system.

- Tunable Artificial Atom at a Supercritically Charged Vacancy in Graphene, J.Mao, Y.Jiang, D. Moldovan, G. Li, K. Watanabe, T. Taniguchi, M. R. Masir, F.M. Peeters, E.Y. Andrei, Nature Physics 12, 545 (2016)
- [2] Observing a Scale Anomaly in Graphene: A Universal Quantum Phase Transition, O. Ovdat, J. Mao, Y.Jiang, E. Y. Andrei, and E. Akkermans Nature communications, 8, 507, (2017)
- [3] Tuning a Circular p-n Junction in Graphene from Quantum Confinement to Optical Guiding, Yuhang Jiang, Jinhai Mao, Dean Moldovan, Massoud Ramezani Masir, Guohong Li, K. Watanabe, T. Taniguchi, Francois M. Peeters and Eva Y. Andrei, Nature Nanotechnology, 12, 1045 (2017)
- [4] Quantum Critical Transition and Kondo Screening of Magnetic Moments in Graphene, Jinhai Mao, Y. Jiang, Po-Wei Lo, D, May, G. Li., GY Guo, F. Anders, T. Taniguchi, K. Watanabe, and E.Y. Andrei, arXiv:1711.06942

Visualizing quantum Hall liquids and their topological boundary modes

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Over the last few years, we have used the scanning tunneling microscope (STM) to visualize a variety of quantum Hall phases. Starting with the realization that local density of states near isolated impurities, can provide us with the ability to directly visualize Landau orbits and the wavefunction of various quantum Hall phases, we have been able to probe a number different phenomena in quantum Hall liquids. We have applied this technique to study quantum Hall phases formed in ultra clean two-dimensional surface states of Bi at high magnetic fields, which provides access to a number of different valley polarized quantum Hall states. This includes quantum Hall nematic phases [1], which break the symmetry of the underlying lattice as well as newly observed evidence for quantum Hall ferroelectric phase [2]. I will describe these experiments as well as new efforts on characterizing the electronic properties of the domain walls between different quantum Hall phases in these systems, which host novel topological edge modes (Luttinger liquids), showing indication of protection from scattering resulting from valley polarization [3]. Finally, if there was time I will also describe the prospects of using STM to probe anyons, which are non-abelian excitations, in fractional quantum Hall phases [4].

- [1] B. Feldman et al. Science 354, 6310 (2016)
- [2] M. Randeria et al. Nature Physics, to appear (2018)
- [3] M. Randeria et al. (2018)
- [4] Z. Papić et al. Physical Review X 8011037 (2018)

Atomic scale imaging of strain-tuned emergent phases of matter

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In many high temperature superconductors, small orthorhombic distortions of the lattice structure result in surprisingly large symmetry breaking of the electronic states, an effect often referred to as nematicity. This symmetry breaking has been observed both microscopically using low temperature STM as well as in macroscopic properties. It has been studied extensively in iron-based superconductors with an orthorhombic crystal structure, where the lattice symmetry is already reduced from four-fold (C_4) to two-fold (C_2).

To directly study the impact of the lattice symmetry and small distortions of the lattice on the electronic structure, we introduce strain STM, enabling in-situ strain tuning of the samples. We image at the atomic scale the influence of the strain-tuned lattice distortions on the correlated electronic states using low temperature scanning tunneling microscopy and spectroscopy [1]. In the iron-based superconductor LiFeAs, a material which in its ground state is tetragonal, with C_4 symmetry, our experiments uncover a new strain-stabilised nematic phase which exhibits a unidirectional charge density wave (CDW) order, an electronic state is apparent in topographic STM images through a characteristic long-range stripe-like modulation of the electronic density of states. We follow the evolution of the superconducting gap as well as this charge-ordered state from the unstrained material with C_4 symmetry through the new nematic phase with C_2 symmetry and CDW order to a state where superconductivity is completely suppressed.

References:

[1] Chi Ming Yim, Christopher Trainer, Ramakrishna Aluru, Shun Chi, Walter N. Hardy, Ruixing Liang, Doug Bonn, and Peter Wahl, *Discovery of a strain-stabilised charge density wave in LiFeAs*, cond-mat:1802.05019 (2018).



Fig 1. Phase diagram of uniaxially strained LiFeAs as a function of strain ε . [1]

Interfacial Superconductivity in 2D Layers of Fe-Chalcogenides on Topological Insulators Studied by Spin-Resolved Scanning Tunneling Spectroscopy

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In this presentation, we will focus on interfacial superconductivity in novel types of heterostructures. In particular, we will present a low-temperature SP-STS study of ultrathin $FeTe_{1-x}Se_x$ (x = 0, 0.5) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in FeTe_{0.5}Se_{0.5} layers of one unit cell (UC) thickness with a transition temperature (T_c) of ~11 K, close to the one of the corresponding bulk system ($T_c \sim 14.5$ K) [1]. Surprisingly, we also find clear evidence for superconductivity up to $T_c \sim 6$ K for one UC thick FeTe layers grown on Bi₂Te₃ substrates [2], in contrast to the non-superconducting FeTe bulk compound which exhibits bicollinear antiferromagnetic (AFM) order in a wide temperature range up to 70 K. Even more surprisingly, detailed investigations of the atomic-scale spin-resolved local density of states by SP-STS reveal that superconductivity in one UC layers of FeTe grown on Bi₂Te₃ appears to spatially coexist with bi-collinear AFM order. By using 3D-vector-resolved SP-STM techniques [3] we find an unusual reorientation of the diagonal double-stripe spin structure at $Fe_{1+v}Te$ thin film surfaces [4]. Moreover, variable-temperature SP-STM studies [5] reveal an enhanced Néel temperature for AFM spin ordering of the ultrathin FeTe films grown on topological insulators [6]. These findings open novel perspectives for theoretical studies of competing orders in Fe-based superconductors as well as for experimental investigations of exotic phases in heterostructures of topological insulators and superconducting layers.

References:

- [1] A. Kamlapure, S. Manna, L. Cornils, T. Hänke, M. Bremholm, Ph. Hofmann, J. Wiebe, and R. Wiesendanger, Phys. Rev. B 95, 104509 (2017):
 "Spatial variation of the two-fold anisotropic superconducting gap in a monolayer of FeSe0.5Te0.5 on a topological insulator".
- [2] S. Manna, A. Kamlapure, L. Cornils, T. Hänke, E. M. J. Hedegaard, M. Bremholm, B. B. Iversen, Ph. Hofmann, J. Wiebe, and R. Wiesendanger, Nature Commun. 8, 14074 (2017):
 "Interfacial superconductivity in a bi-collinear antiferromagnetically ordered FeTe monolayer on a topological insulator".
- [3] S. Meckler, M. Gyamfi, O. Pietzsch, and R. Wiesendanger, Rev. Sci. Instrum. 80, 023708 (2009): "A low-temperature spin-polarized scanning tunneling microscope operating in a fully rotatable magnetic field".
- [4] T. Hänke, U. R. Singh, L. Cornils, S. Manna, A. Kamlapure, M. Bremholm, E. M. J. Hedegaard, B. B. Iversen, Ph. Hofmann, J. Hu, Z. Mao, J. Wiebe, and R. Wiesendanger, Nature Commun. 8, 13939 (2017):
- "Reorientation of the diagonal double-stripe spin structure at $Fe_{1+y}Te$ bulk and thin film surfaces".
- [5] J. Warmuth, M. Bremholm, Ph. Hofmann, J. Wiebe, and R. Wiesendanger, submitted: "Domain imaging across the magneto-structural phase transition in Fe_{1+v}Te".
- [6] U. R. Singh, J. Warmuth, A. Kamlapure, L. Cornils, M. Bremholm, Ph. Hofmann, J. Wiebe, and R. Wiesendanger, submitted:

"Enhanced spin ordering temperature in ultrathin FeTe films grown on a topological insulator".

Multifractal superconductivity in single-layer NbSe₂

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Single layers of transition metal dichalcogenides are ideal systems for exploring the interplay between 2D superconductivity and localization effects. Here we present a comprehensive characterization of the superconducting state of single-layer NbSe₂ ($T_c = 2$ K [1]) in the vicinity of the critical point of the superconducting-insulator (SIT) transition by means of low-temperature (1.1 K) scanning tunnelling microscopy and spectroscopy (STM/STS). Our STS measurements show that even the weak intrinsic disorder present in the 2D material triggers strong spatial fluctuations in the width, depth and coherence peak heights of the SC gap. Spatially resolved mapping of these observables reveal that such fluctuations display in all cases patterns with well-defined wavelength of ~7 Å, nearly coincident with that of the quasiparticle oscillations visible near E_F [2]. Statistical analysis the local SC widths and the coherence peak heights reveal log-normal distributions, and for the former a two-point correlation function that decays as a power-law, both signatures of the multifractal character of the superconducting eigenstates [3]. This superconducting state offers a novel platform to tune and control superconductivity in quasi two-dimensional quantum materials.





Figure: Spatially resolved fluctuations of the local order parameter (SC width) in single-layer NbSe₂ at 1 K.

0.8 mV

- [1] Ugeda, et al., Nat. Phys. 12, 92 (2015).
- [2] Argüello, et al., PRL 114, 037001 (2015).
- [3] J. Mayoh and A. M. García-García, PRB 92, 174526 (2015).

Visualizing the electronic structure of atomically thin high-Tc cuprate crystals

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The role of dimensionality in high Tc superconductivity is an interesting issue: after all, many of the high Tc superconductor have layered atomic structures, and yet the link between the high Tc superconductivity and the two-dimensional nature of the crystal structure remains elusive^{1,2}. Here, we fabricate few-layer Bi₂Sr₂CaCu₂O_{8+\delta} samples, and use scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) to investigate the electronic structure, such as superconducting gap, pseudo gap and charge order, in $Bi_2Sr_2CaCu_2O_{8+|delta}$ in the 2D limit.

- [1] Anderson, P. W. c-Axis Electrodynamics as Evidence for the Interlayer Theory of High-Temperature Superconductivity. Science 279, 1196–1198 (1998).
- Gerber, S. et al. Three-dimensional charge density wave order in YBa2Cu3O6.67 at high magnetic fields. Science [2] 350, 949–952 (2015).



Fig 1. (a) Atomic structure model of $Bi_2Sr_2CaCu_2O_{8+|delta}$. (b) Optical image of a mechanically cleaved 1L $Bi_2Sr_2CaCu_2O_{8+\mid delta}$ accessed by STM tip (tip is sketched).

Probing magnetic interactions between Cr adatoms on the Bi₂Pd superconductor

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We show that the magnetic ordering of coupled atomic dimers on a superconductor is revealed by their intra-gap spectral features. Chromium atoms on the superconductor Bi2Pd surface display Yu-Shiba-Rusinov bound states, detected as pairs of intra-gap excitations in tunneling spectra. By means of atomic manipulation with a scanning tunneling microscope's tip, we formed Cr dimers with different arrangements and found that their intra-gap features appear either shifted or split with respect to single atoms. The spectral variations reveal that the magnetic coupling of the dimer changes between ferromagnetic and antiferromagnetic depending on its disposition on the surface, in good agreement with density functional theory simulations. The striking qualitative difference between the two magnetic orderings proves that intra-gap state spectroscopy gives an accurate information of exchange interactions on the atomic scale.

References:

[1] Choi, D.-J., et al. Phys. Rev. Lett. 120, 167001 (2018).

Novel theoretical approaches to extract information from STM and AFM experiments in 2D materials

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STM and AFM with CO-metal tips are the tools of choice to characterize 2D materials at the atomic scale. Together with some basic theoretical principles and relatively simple computational approximations, they can provide almost direct access to the electronic and magnetic properties (STM) and the structure of 2D materials (AFM). Here, we'll discuss how a more sophisticated theoretical modelling can help to extract quantitative information from the experiments and extend the SPM capabilities, including possibly chemical identification.

In the case of STM, a better description of the transport process (using, for example, Green's function techniques) and a proper account of the tip paves the way to unveil the atomic structure and characterize the electronic states at the boundary between a graphene (G) zigzag edge and a metal step [1]. This same approach helps to understand the tunable transparency in G/Cu and to provide a comprehensive picture of the G-metal coupling with atomic precision and high energy resolution [2], with important implications for the accurate description of van der Waals interactions. A proper simulation of the current beyond the standard Tersoff-Hamman approach is also needed to reproduce quantitatively the trends observed in the STM apparent corrugation of the different moiré structures in G/Rh [3]. Theory also helps to understand how the G electronic properties can be further tuned combining N-doping with oxygen intercalation [4-6].

So far, most of the theoretical work to understand the AFM contrast with CO tips has been based on simple but efficient models that rely on pair-wise potentials for the calculation of the total tip-sample interaction. A more fundamental but still efficient approach can be developed from information extracted from first-principles calculations [7]. This model properly includes the electrostatic field created by a CO-metal tip [8] and describes both the intra- and intermolecular contrast observed in a hydrogen-bonded monolayer of triazine molecules [9]. Here, we go a step further and demonstrate that all the relevant interactions can be computed solely from the charge densities of the sample and the tip while retaining DFT accuracy [10]. Our model captures the subtle effects introduced by the stoichiometry and bonding environment in the image contrast of a given chemical specie in different molecules, reproduces the contrast associated with different bond orders, disentangles the contribution of electrostatics and Pauli repulsion, and provides insight into the highly controversial role of charge redistribution in the imaging of Hydrogen bonds.

- [1] P. Merino et al., ACS Nano 8, 3590-3596 (2014).
- [2] H. Gonzalez-Herrero et al., ACS Nano 10, 5131 (2016).
- [3] A. Martin-Recio et al., Nanoscale 7, 11300 (2015).
- [4] C. Romero-Muñiz et al., Carbon 101, 129 (2016).
- [5] A. Martín-Recio, et al., Nanoscale 8, 17686 (2016).
- [6] A. Martín-Recio, et al., Carbon 130, 362 (2018)
- [7] M. Ellner et al, Nano Letters 16, 1974 (2016).
- [8] M. Ellner, P. Pou and R. Perez, Chapter 15, p. 465-497, in S. Sadewasser and T. Glatzel (eds.), *Kelvin Probe Force Microscopy*. (Springer, 2018).
- [9] M. Ellner, P. Pou and R. Perez, Phys. Rev. B 96, 075418 (2017).
- [10] M. Ellner, P. Pou and R. Perez, submitted (2018).

Tailoring charge and spin transport at molecule/layered material interfaces

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New functionalities can be tailored in molecular devices by specifically designing the hybrid interfaces between the electrode and the molecules. Recently, the use of layered materials with unique surface properties as electrodes has offered new intriguing possibilities in this regard. Here, I will present a few prominent experimental examples that I modelled by means of Density Functional Theory (DFT) simulations.

In first place, I will discuss charge transport at graphite/molecule interfaces showing that covalently and non-covalently attached molecules exhibit a large rectification that occurs in opposite directions for the two cases. Moreover, the functionalization of the graphite surface via the C-C direct bond results in a room temperature-stable and precisely-defined contact ensuring reproducibility in molecular devices under ambient conditions [1]. Extensions of this study to include magnetic molecules are currently under investigation.

Secondly, we will discuss how molecules can be used to modify the spin texture of metallic and semiconducting surfaces that have a large spin-orbit coupling. The specific case of functionalized phthalocyanine molecules on the topological insulators Bi₂Se₃[2] will be discussed along with some preliminary results for other systems. Furthermore, possible implications in the context of spin-charge conversion effects will be briefly mentioned.

References:

- [1] [1] A.V. Rudnev, V. Kaliginedi, A. Droghetti, H. Ozawa, A. Kuzume, M. Haga, P. Broekmann, I. Rungger, Science Advances3, e1602297 (2017).
- [2] [2] S. Jakobs, A. Narayan, B. Stadtmüller, A. Droghetti, I. Rungger, Y.S. Hor, S. Klyatskaya, D. Jungkenn, J.Stöckl, M. Laux, O.L.A. Monti, M. Aeschlimann, R.J. Cava, M. Ruben, S. Mathias, S. Sanvito, M. Cinchetti, Nano Lett. 15, 6022(2015).



Fig 1. (a) Bias-dependent conductance of the graphite/molecule/Au junctions for DMAB and PPD molecules obtained from both experiment (symbols) and theory. (b) Illustration of rectification behaviour in opposite direction for covalent DMAB-graphite and non-covalent PPD-graphite attachment (Figure adapted from reference [1]).



Fig 2. Angle resolved photo-emission spectrum(ARPES) and density of states calculated by DFT for the interface between Bi₂Se₃ and H₂Pcsmolecules(Figure adapted from reference [2]).

Non-Covalent Control of Spin-State in Metal-Organic Complex by Positioning on N-Doped Graphene and Its SPM Discrimination

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Nitrogen doping of graphene significantly affects its chemical properties, which is particularly important in molecular sensing and electrocatalysis applications. However, detailed insight into interaction between different N-dopants and molecules on an atomic scale is currently lacking. Here, we demonstrate control over the spin state of a single iron(II) phthalocyanine molecule by its positioning on N-doped graphene. The spin transition was driven by combination of non-covalent interactions between surface and molecule and hybridization of the d-orbitals of iron and the p_z orbital of a single graphitic nitrogen. High-resolution atomic force microscopy imaging with a CO-functionalized tip showed that the transition was characterized by a distinct sub-molecular contrast over molecules located on pristine graphene and near to the N-dopant for the singlet and triplet spin states, respectively. This work demonstrates the unique capability of the imaging technique to discriminate between different spin states of single molecules. Moreover, it presents a method for triggering spin state transition and tuning the electronic properties of molecules through weak noncovalent interaction with suitably functionalized graphene.



Fig 1. (a) STM images acquired after steps of controlled lateral manipulation of FePc on N-doped graphene. (b-c) dI/dV spectra acquired at the center of FePc on pristine graphene (blue) and on a N-dopant (red) indicating the impact of the dopant in the electronic structure of molecules.

Electronic interaction between organic molecules and graphene

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Tailoring the properties of graphene is of fundamental interest to uncover new functionalities and open new opportunities for graphene based applications. Among the strategies explored to achieve this goal, substitutional doping and molecular functionalization have focused tremendous efforts. In this context, nitrogen doping obtained by replacing some carbon atoms by nitrogen atoms appears to be particularly interesting as it allows to perform n-doping with minor structural perturbations. This chemical doping can also modify the interaction of graphene with organic molecules that can be exploited for sensing or catalysis. To probe this effect at the molecular level, scanning tunneling microscopy and spectroscopy experiments have been performed on model systems with electron donor (porphyrin) [1,2] and electron acceptor molecules [3] adsorbed on multilayer pristine and doped graphene on SiC(000-1). Local spectroscopy allows to measure resonances arising from the molecular states and to reveal the electronic coupling and charge transfer between the molecules and the graphene. On doped graphene, a local modification of the charge transfer between molecules and graphene occurs at the doping sites. Recent measurements on electron acceptor molecules show such local modification of the charge transfer. In addition, the STS measurements also show that the electric field between the tip and graphene can modify the charge transfer. This effect provide a route to tune the electronic interaction between molecules and graphene.

References:

- [1] V. D. Pham et al., ACS Nano 8, 9403 (2014)
- [2] V. D. Pham et al., Sci. Rep. 6, 24796 (2016)
- [3] V. D. Pham et al., in preparation



Fig 1. Scanning tunneling microscopy image of a porphyrin molecular island on nitrogen doped graphene [2].
Giant tuning of graphene's pseudospin polarization and valley splitting by a scanning tunneling microscope

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Graphene, the first two-dimensional material, provides two extra binary degrees of freedom, - sublattice and valley -, which are adequately described as a pseudospin. The sublattice pseudospin is chiral with respect to the Dirac-type momentum, such that it mimics the relativistic real spin completely. Here, I firstly show that application of large pseudomagnetic fields \underline{B}_{ps} (~ 1000 T) can be used to polarize the sublattice pseudospin up to 40 %. Therefore, the van-der Waals force of an STM tip is exploited, which locally lifts graphene from the SiO₂ substrate and, thus, induces huge strain gradients, i.e. $|\underline{B}_{ps}|$ (Fig. 1, top). The resulting sublattice imbalance can be directly read from STM images and turns out to be in excellent agreement with analytic calculations based on molecular dynamics revealing the induced strain patterns [1].

Secondly, the valley degree of freedom is tuned using a quantum dot induced by the tip potential in combination with an external B field (Fig. 1, bottom) [2]. The laterally changing orientation of graphene's C atoms with respect to the B and N atoms on an angularly aligned BN substrate changes the valley splitting of the confined states continuously. This eventually leads to a tunable inversion of the valley splitting on nm length scales. Again, we provide excellent

agreement with calculations, here, based on density functional theory combined with a tight binding model.

- [1] A. Georgi et al., Nano Lett., 17, 2240 (2017).
- [2] N. Freitag et al., Nano Lett., 16, 5798 (2016), arXiv:1708. 09170 (Nat. Nanotechnol., accepted)

Tunable Strain Solitons in Transition Metal Dichalcogenides

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In a bilayer van der Waals material, the application of differential strain between the layers can lead to the formation of strain "solitons". Such solitons are one-dimensional lines where there is a phase slip of one lattice constant between the two layers that comprise the bilayer. I will describe scanning tunneling microscopy experiments of such strain solitons in transition-metal dichalcogenides. Using a piezo-driven apparatus, we describe a technique by which uniform as well as differential strain can be applied to single crystal materials with arbitrarily large achievable strains. We apply this to a single crystal of semiconducting MoSe2 which has a single freely-standing monolayer on the surface. We describe the controllable application of strain and the production of strain solitons in this system. We find that strain solitons form along the principal axes of the crystal, and in the case of an arbitrary direction of applied strain the solitons form elongated, quasi-periodic, hexagonal patterns for strain relief. At the vertices of each hexagon, a Y junction is formed, and the vertex of the junction is under triaxial strain. STM spectroscopy measurements show the presence of Landau levels in the Y-junction vertex, with an effective magnetic field of about 300 Tesla.

Visualizing the Interplay between Spatial and Magnetic Confinement in Graphene Quantum Dots

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At the heart of the wave nature of quantum mechanics is the quantization of energy due to quantum confinement when the particle's de Broglie wavelength becomes comparable to the system length scale. Ouantization can occur through spatial constraints or by large magnetic fields via cyclotron motion. Quantum dots (QD), which resemble artificial atoms, offer an ideal platform for studying quantum confinement. Historically, the majority of QD systems investigated have been based on semiconductor heterostructures. Recently, the ability to apply local nanometer scale gate potentials in graphene heterostructures has enabled the creation of QDs for Dirac particles. Graphene QDs are formed inside circular p-n junctions [1,2], where one has detailed control of electron orbits by means of local gate potentials and magnetic fields. In this talk, I describe scanning tunneling spectroscopy measurements of the energy spectrum of graphene QDs as a function of energy, spatial position, and magnetic field. In zero field, the Dirac quasiparticles are confined by Klein scattering at large incident angle at the *p*-*n* junction boundary. The confined carriers give rise to an intricate eigenstate spectrum, characterized by radial and angular momentum quantum numbers, effectively creating a multi-electron artificial atom [1]. Applying a weak magnetic field results in a sudden and giant increase in energy for certain angular momentum states of the QD, creating a discontinuity in the energy spectrum as a function of magnetic field [2]. This behavior results from a π -Berry phase associated with the topological properties of Dirac fermions in graphene, which I show can be turned on and off with magnetic field. With increased applied magnetic field, the OD states are observed to condense into Landau levels, providing a direct spatial visualization of the transition from spatial to magnetic confinement in these artificial graphene atoms. We determine the Landau level spatial properties, which show a "wedding cake" profile arising from interaction effects, as predicted by theory, and can now can be directly mapped and visualized in a solid-state system for the first time [3].

References:

- [1] Y. Zhao, J. Wyrick, F. D. Natterer, J. F. Rodriquez-Nieva et al., Science 348, 672 (2015).
- [2] F. Ghahari, D. Walkup, C. Gutiérrez, J. F. Rodriguez-Nieva et al., Science 356, 845 (2017).
- [3] C. Gutiérrez, D. Walkup, F. Ghahari, Cyprian Lewandowski et al., (submitted).



Fig 1. (A) Schematic of the potential profile formed by a *p*-doped graphene center region and *n*-doped background, created by ionizing impurities in the underlying hBN insulator. (B) Differential conductance map vs. radial spatial position obtained from an angular average of an *xy* grid of spectra obtained over the graphene resonator. $m = \pm 1/2$ states appear in the center at r = 0, whereas states with higher angular momentum occupy positions away from center in arcs of increasing *m* values and common *n* value. The solid blue line shows a parabolic potential confining the carriers in the graphene QD. From Ref. [2].

Quantum confinement of graphene massless Dirac quasiparticles

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The possibility to pattern graphene has attracted huge interest among the scientific community, as it allows the selective modification of the electronic properties of this material. However, the creation of graphene structures bellow 10 nanometer precision still remains a challenge [1]. Some outstanding advances have been recently achieved with the creation of graphene quantum dots by the local manipulation of defect charge within an insulating substrate beneath a graphene monolayer [2, 3]. However, the graphene quasiparticle confinement there was limited due to the existence of Klein tunneling [4] and they only showed circular shaped dots, probably imposed by tip geometry.

In this work we take advantage of our recent finding that hydrogen atoms can be manipulated at will over the surface of graphene (they can be moved, placed, desorbed) by using a STM tip [5]. We go one step further and present a new methodology to create graphene nanopatterns with sub-nanometer precision by the collective manipulation of a large number of H atoms with the STM tip. We measure the local density of states inside the so created graphene nanostructures to demonstrate that they confine graphene quasiparticles in a very efficient way, giving rise, for example, to perfectly defined energy band gaps.

References:

- [1] J. Guttinger et al., Reports on Progress in Physics, 75, 126502 (2012).
- [2] J. Lee *et al.*, Nature Physics. **12**, 1032 (2016).
- [3] F. Ghahari *et al.*, Science **356**, 845 (2017)
- [4] M.I. Katnelson et al., Nature Physics. 2, 620625 (2006).
- [5] H. González-Herrero et al., Science, 352, 437 (2016)



Figure 1. STM image showing 3 triangular graphene quantum dots with sides of 22, 11 and 6 nm. The dot edges are made by the collective manipulation of H atoms adsorbed on a graphene surface. Image size $64x44nm^2$

Landau quantization in graphene/transition metal dichalcogenides probed at the local scale

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The perspective of revolutionizing graphene nanoelectronics by the fabrication of 2D stacked systems from the group of transition metal dichalcogenides (TMDs) has sparked the interest of scientists and engineers alike [1]. The proximity of graphene to the layered van der Waals materials allows for a considerable modification and tuning of the electronic properties of graphene including its spin-orbit interaction (SOI) strength, as has been demonstrated in recent magneto transport experiments [2,3].

Here, we present the successful preparation of layered systems of a graphene monolayer on tungsten diselenide (WSe₂), niobium diselenide (NbSe₂) and molybdenum diselenide (MoSe₂) accomplished by the wet chemical transfer of CVD graphene on TMD single crystals. The structural properties of the composite system are investigated by means of low-temperature scanning tunnelling microscopy (STM) in ultra-high vacuum (UHV). Hereby different Moiré superstructures resulting from the lattice mismatch with the underlying substrate are observed that confirm the successful transfer process. Atomically resolved imaging furthermore allows the identification of localised defects in both underlying substrate as well as the graphene monolayer itself.

The subsequent investigation with regard to the electronic properties is carried out with the help of scanning tunnelling spectroscopy (STS) in high magnetic fields. Pronounced Landau level sequences observed in STS confirm a rather weak coupling between graphene and substrate. A detailed analysis of the Landau level spectrum allows the determination of the Fermi velocity as well as the doping level of graphene, showing strong spatial variations on a scale of 100 nm. The observation of an additional splitting of each Landau level peak into subpeaks is discussed with regard to a possible TMD substrate induced SOI in graphene.

Angle-resolved photoemission spectroscopy measurements complement the local investigations of the electronic properties of graphene and confirm the characteristic linear dispersion of graphene as well as the presence of TMD bulk bands.

- [1] A. K. Geim, and I. V. Grigorieva, Nature 499, 419 (2013)
- [2] Z. Wang et al., Nature Comm. 6, 8339 (2015)
- [3] Z. Wang et al., Phys. Rev. X 6, 041020 (2016)

Electric Field Effect on the Intramolecular Hydrogen Transfer of Phthalocyanine Molecule

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Atomic level understanding of the electric field effect on a single molecule, especially on its chemical and electrical properties, is crucial to develop molecular electronics. STM can spatially resolve single atoms and prove the physical and chemical properties by controlling tip-sample distance, bias voltage and tunneling current. However, these three parameters are strongly entangled so that each parameter is actually determined by the other two. In other words, the electric field effect cannot be recognized separately by simple STM measurement. We overcome this challenge by combining the graphene field effect transistor and the gate-tunable STM. Using the gate-tunable STM, the graphene substrate is electrostatically doped to alter the charge carrier density, which varies tip-sample distance without varying the number of the injected electrons or their relative potential. Applying this method, we demonstrate the electric field effect on the intramolecular H transfer, i.e. tautomerization reaction, in H₂-phtalocyanine molecule on graphene field effect transistor using gate-tunable STM at 4K. Applied back gate increase the charge carrier density on the graphene surface which induce the tip-retraction in constant current mode, i.e. reduction of the electric field. As the electric field is reduced the frequency of tautomerization decreased. Our theoretical calculation reveals that the activation barrier of tautomerization is increased when the electric field is decreased. The energy level shift, variation of charge carrier density in the relation to the applied back gate voltage will be discussed in detail.

Electronic Structure and Electron Dynamics in Two-Dimensional Dirac Materials

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Artificial two-dimensional (2D) materials, such as graphene or single-layer transition metal dichalcogenides, permit the realization of massless and massive Dirac fermions. A special feature of the 2D materials is that their electronic properties, for instance their band gap, can be strongly influenced by either their dielectric environment or by the excited carrier density in the material. Here we exploit this to achieve a static and dynamic change in the electronic properties of 2D materials such as graphene and single layer WS_2 . We also make use of the electronic structure's tunability in order to address some fundamental questions concerning the electronic self-energy in solids.

Charge Order in NbSe₂

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Niobium diselenide has long served as a prototype of two-dimensional charge ordering, believed to arise from an instability of the electronic structure analogous to the one-dimensional Peierls mechanism. Despite this, various anomalous properties have been experimentally identified which cannot be explained by Peierls-like weak-coupling theories. We instead present a model based on strong electron-phonon coupling, taking into account both the full momentum and orbital dependence of the coupling matrix elements [1]. Both are necessary for a consistent description of the full range of experimental observations. By including strain in the model we explain the observed coexistence of domains of geometrically distinct charge-ordering patterns, as seen by surface scanning tunnelling microscopy [2,3]. In collaboration with the experimental group of I. Zeljkovic we have identified that both the geometries and periods of the charge-ordering patterns can be addressed controllably with applied strain [4]. In ongoing work with L. Chirolli we propose explanations for a number of recent unexplained observations using scanning tunneling probes in single monolayers of the material [5].

- [1] F. Flicker and Jasper van Wezel, Charge Order from Orbital Dependent Coupling Evidenced by NbSe₂, Nature Communications 6, 7034 (2015)
- [2] F. Flicker and Jasper van Wezel, Charge Ordering Geometries in Uniaxially-Strained NbSe2, Physical Review B 92, 201103 (Rapid Communications) (2015)
- [3] F. Flicker and Jasper van Wezel, Charge order in NbSe2, Physical Review B 94, 235135 (2016)
- [4] S. Gao, F. Flicker, R. Sankar, H. Zhao, Z. Ren, B. Rachmilowitz, S. Balachandar, F. Chou, K. Burch, Z. Wang, J. van Wezel and I. Zeljkovic, Atomic-Scale Strain Manipulation of a Charge Density Wave under peer review at Proceedings of the National Academy of Sciences
- [5] M. M. Ugeda et al., Characterization of collective ground states in single-layer NbSe₂, Nature Physics 12, 92-97 (2016)



Figure 1: Left: calculated phonon softening giving a good match to the experimental QCDW. Middle: density of states measured by scanning tunneling spectroscopy (blue points, from [Soumyanarayanan et al. PNAS 110, 1623 (2015)]) and our model's prediction (red curve). Right: calculated phase diagram as a function of temperature and strain σ . All plots from [3].

Non-monotonic thickness dependence of the charge density wave order parameter in VSe₂

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We present a detailed scanning tunneling microscopy (STM) study of the thickness and temperature dependences of the charge density wave (CDW) order parameter in bulk and *in situ* exfoliated VSe₂ [1]. We show that mapping the real-space charge order over a broad and well-characterized thickness range provides essential insight. The 4x4 in-plane charge order is preserved down to the thinnest flakes, however with strongly varying modulation strength. We introduce a robust derivation of the local order parameter and transition temperature based on the real space charge modulation amplitude measured by STM (Fig.1a). Both quantities exhibit a striking non-monotonic thickness dependence (Fig.1b) that we explain in terms of a 3D to 2D dimensional crossover in the Fermi surface topology [2]. Modeling further shows the enhancement of the order parameter in the thinnest specimen to result from confinement and not from a change in the coupling strength. This finding highlights thickness as a true tuning parameter of the electronic ground state.

- [1] Á. Pásztor et al. Review of Scientific Instruments 88, 076104 (2017).
- [2] Á. Pásztor et al. 2D Mater. 4, 041005 (2017).



Fig 1. (a) $9x9 \text{ nm}^2$ high resolution STM micrograph at 77.6 K of the atomic lattice and CDW modulation on a VSe₂ nanoflake. (b) Thickness dependence of the CDW order parameter ψ calculated from the charge modulation imaged by STM. The error bars correspond to the dispersion of ψ across many different STM images at a given thickness.

CDW temperature in bulk and monolayer transition metal dichalcogenides from first-principles

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A charge-density wave (CDW) transition is a lattice dynamical instability that induces a modulation of the charge density. Transition metal dichalcogenides (TMDs) show a very interesting and diverse phase diagram where CDW and superconducting states might appear. The interaction between the CDW and superconductivity is still under intense debate.

The interest on TMDs has attracted a great deal for attention since it was shown that these layered materials could be exfoliated down to the monolayer and provide a wide of range of 2D materials [1]. Whether the dimensionality reduction affects the CDW is not clear at the moment as contradictory results have been recently reported: while optical and electrical transport measurements suggest the CDW temperature is strongly enhanced in the monolayer [2], scanning tunnelling microscopy suggests it is practically unaffected [3]. This apparent contradiction calls for a theoretical first-principles study of the CDW temperature in both bulk and monolayer TMDs.

A CDW transition is a second-order structural phase transition in which the frequency of a phonon mode of the high-temperature phase is strongly suppressed with lowering the temperature, collapsing to 0 at the CDW transition temperature. This triggers the CDW state. Thus, in order to determine the CDW temperature, ab initio methods need to calculate the temperature dependence of the phonons at the high temperature phase and see at which temperature the frequency of the CDW mode vanishes. This, unfortunately, is a daunting task, as the standard harmonic approximation predicts that the phonons of the high-temperature phase are unstable and cannot explain any temperature dependence of the phonon frequencies. Moreover, any perturbative approach is not viable and a non-perturbative treatment of anharmonicity becomes necessary, not a trivial task for first-principles approaches.

Making use of the stochastic self-consistent harmonic approximation (SSCHA) [4,5] that we have developed, we can accurately calculate for the first time the temperature dependence of the phonons even in the nonperturbative anharmonic regime and determine the CDW transition temperature. Here, we present what to our knowledge is the first fully ab initio calculation of a CDW temperature both in bulk and monolayer NbSe2 and NbS2. Our calculations are crucial to understand the interaction of the CDW with the dimensionality, and shine light into the experimental controversy.

- [1] K.S. Novoselov, et al., PNAS 102, 10451 (2005)
- [2] X. Xi, et al., Nature Nanotechnology 10, 765 (2015)
- [3] M.M. Ugeda, et al., Nature Physics 12, 92 (2016)
- [4] I. Errea, et al., PRB 89, 064302 (2014)
- [5] R. Bianco, et al., PRB 96, 014111 (2017)

Electronic Correlations and Competing Interactions in Two-Dimensional Materials

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The interplay of Coulomb and electron-phonon interactions with thermal and quantum fluctuations facilitates rich phase diagrams in two-dimensional electron systems. Layered transition metal dichalcogenides (TMDCs) hosting charge, excitonic, spin and superconducting order form an epitomic material class in this respect. Here, we analyze the interplay of short- and long-range Coulomb as well as electron-phonon interactions in monolayers of 2d materials. We show that the combination of these interactions causes electronic correlations that are fundamentally different to what would be expected from the interaction terms separately, as we illustrate with the example of NbS₂ in the H-phase [1]. We then analyze the competition of spin, charge and superconducting order in the entire family of metallic TMDCs and show that particularly the Nb-based compounds are at the verge between spin and charge order. Finally, we consider recently synthesized 1T-NbSe₂ [2] and discuss the interplay of lattice distortions, non-local exchange, and Coulomb interactions to pinpoint the nature of possible correlated insulating states in this material.

- [1] E. G. C. P. van Loon, M. Rösner, G. Schönhoff, M. I. Katsnelson, T. O. Wehling, arXiv:1707.05640 (2017).
- [2] Y. Nakata, K. Sugawara, R. Shimizu, Y. Okada, P. Han, T. Hitosugi, K. Ueno, T. Sato, and T. Takahashi, NPG Asia Mater 8, e321 (2016).



Fig 1. Magnetic susceptibilities of H-phase TMDCS. If interactions are taken into account (left panel) there is strong Stoner enhancement and magnetic order in the Nb and V-based compounds.

Chiral spin texture in the charge-density-wave phase of the correlated metallic Pb/Si(111) monolayer

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Group IV adatoms on group IV semiconductors (111) surfaces represent an important research topic[1]. In fact it is known, those materials present a lot of exotic phenomena, such as many reversible phase transitions as a function of temperature[2,3], magnetic orderings[4,5], metal-insulator transitions[6,7] and also superconductivity[8].

Depending on the coverage there are many possible reconstructions and related physical properties. At room temperature 1/3 ML coverage of Pb (or Sn) grown on top of Si(111) (or Ge(111)) displays an isoelectronic $\sqrt{3} \times \sqrt{3}$ -R30° reconstruction. The host atoms occupy the T4 sites atop the substrate surface in an hexagonal array [6], the so-called α -phase (see Fig.1a). The three Si dangling bonds in the top Si layer next to the metal atom are saturated and a free unsaturated electron is left at each T4 site. Thus these systems are expected to present a half-filled surface band well separated from the substrate bands. This expectation is however in contrast with experimental evidences of an insulating ground state in Sn on Ge(111) [6] and Si(111) [9].

The reason of this behaviour has been attributed to electronic correlations [7]. At low temperature the situation is complicated by the presence in most systems of a reversible structural transition from $\sqrt{3} \times \sqrt{3}$ to 3×3 periodicity [2,3,10,11]. Although its origin has been extensively debated, it is still not clear yet whether this transition is due to the freezing of an out-of-plane phonon mode [12] or produced by long-range electronic correlations [13], both favouring a charge-density-wave having the so-called 1Up-2Down atoms configuration (see Fig.1a).

In this work we study the 1/3 ML α -Pb/Si(111) by scanning tunneling microscopy/spectroscopy (STM/STS) and by fully-relativistic Density Functional Theory. Experimental results down to 300 mK reveal the 3×3 ground-state to be a correlated metal not undergoing a Mott transition. It is characterized by a highly depressed density of states at the Fermi level (EF) where well-defined quasiparticles exist, resulting in two large Fermi surfaces with dominant in-plane spin polarization and opposite helicities.

We demonstrate Pb-substrate interaction, non-collinear spin-orbit coupling and correlation effects are all mandatory ingredients to correctly describe the electronic structure of the 1/3 ML Pb/Si(111) surface and its reconstructions. We have found that the low-temperature ground-state of the 3×3 reconstruction is a strongly correlated metal with well developed lower and upper Hubbard bands coexisting with a charge-density-wave phase. By comparing calculated quasiparticle interference with Fourier transform of STS data, we demonstrated the occurrence of two large hexagonal Fermi surfaces with in-plane spin polarization and opposite helicities.

- [1] P. Estrup and J. Morrison: Surface Science, vol. 2, pp. 465 472, 1964.
- [2] J. M. Carpinelli, H. H. Weitering, E. W. Plummer, and R. Stumpf: Nature, vol. 381, pp. 398-400, 1996.
- [3] J. M. Carpinelli et al. : Phys. Rev. Lett., vol. 79, pp. 2859–2862, 1997.
- [4] G. Li et al. : Nat Commun, vol. 4, p. 1620, 2013.
- [5] J.-H. Lee, H.-J. Kim, and J.-H. Cho: Phys. Rev. Lett., vol. 111, p. 106403, 2013.
- [6] R. Cortes et al. : Phys. Rev. Lett., vol. 96, p. 126103, 2006.
- [7] G. Profeta and E. Tosatti: Phys. Rev. Lett., vol. 98, p. 086401, 2007.
- [8] T. Zhang et al. Nature Physics, vol. 6, pp. 104–108, 2010.

- [9] S. Modesti et al. : Phys. Rev. Lett., 98, 126401 (2007).
- [10] I. Brihuega, O. Custance, R. Pérez, and J. Gomez-Rodríguez: Phys.Rev.Lett., 94, 046101 (2005).
- [11] I. Brihuega, O. Custance, M. Ugeda, and J. Gomez-Rodríguez: Phys.Rev.Lett., 75, 155411 (2007).
- [12] P. Cudazzo, G. Profeta, and A. Continenza, Surface Science, 602, 747 (2008).
- [13] P. Hansmann, T. Ayral, L. Vaugier, P. Werner, and S. Biermann: Phys. Rev. Lett., 110, 166401 (2013).



Fig 1. (a) Top: top-view of the high-temperature $\sqrt{3} \times \sqrt{3}$ R30° (red) and low-temperature 3×3 (blue) unit cells of 1/3 ML Pb/Si(111). Bottom: Side-view of the 3×3 α-phase. Small (large) circles represent Si (Pb) atoms. (b) Symmetrized Fourier transform of a 60×60 nm2 dI/dV (V = 0) map measured by STS at T=0.3 K and B=0.5 T, corresponding to quasiparticle interference at E=EF. (c) Calculated quasiparticle interference map at E=EF assuming pure scalar impurity scattering.

Atomic and electronic structures of 2D electronic materials and their heterostructures

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The emerging atomic layer materials offer a remarkably wide range of building blocks of nanostructures ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). Key advantages of these van der Waals materials include a broad span of energy gaps, flexibility of stacking different types of materials to form heterostructures, tunability in material properties by doping and strain, and the relative ease of integration with other electronic and photonic devices. This talk will be focused on the our recent work in probing the atomic and electronic structure of transition metal dichalcogenides (TMDs) and their heterostructures, including both vertical and lateral structure.

I will first introduce a comprehensive form of scanning tunneling spectroscopy (STS) which allows us to probe not only the quasi-particle band gaps but also the critical point energy locations and their origins in the Brillouin Zone (BZ) can be revealed using this comprehensive form of STS. By using this new method, we unravel the systematic trend of the critical point energies for TMDs due to atomic orbital couplings, spin-orbital coupling and the interlayer coupling. By using the vertically stacked MoS2/WSe2, I will show how interlayer coupling can be used as a new designing parameter to create a lateral 2D electronic superlattices. I will then turn attention to MoS2/WSe2 lateral heterostructure where I will show a novel method to probe 2D strain tensor and how the strain changes the band profile as well as the band alignment at the interface.

Quantization effects and spin charge separation in metallic wires: mirror twin boundaries in monolayer MoS₂ on graphene

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Graphene and monolayers of hexagonal boron nitride on Ir(111) are superior substrates for the synthesis of new materials, such as organometallic sandwich molecular wires, oxide thin films and transition metal dichalcogenide layers.

In this contribution I will discuss a two-step molecular beam epitaxy synthesis with elemental sulfur enabling the growth of clean, almost defect-free and well-decoupled layers of transition metal disulfides [1]. Using scanning tunneling microscopy, low energy electron diffraction, and angle-resolved photoemission spectroscopy we optimize the growth process, provide insight into the growth as well as annealing mechanisms, and characterize the global electronic structure of the layers, using MoS_2 as a paradigm.

With the help of scanning tunneling spectroscopy, ab initio calculations and analytical modeling we investigate one-dimensional strongly correlated metallic states confined within two different types of twin boundaries in monolayers of MoS_2 . Experimentally, these states are characterized by clear length-dependent quantization effects, by a gap in the density of states of the order of 100 meV around the Fermi level, and by

an incommensurate modulation of the measured density of states along the wire which extends deep into the discrete states below and above the Fermi level. We highlight the relevance of spin-charge separation to understand the observed complex electronic structure and critically discuss our results in the light of previous related research [2-4].

Contributions to this work by Wouter Jolie, Joshua Hall, Clifford Murray, Tobias Wekking, Carsten Busse, Fabian Portner, Philipp Weiß, Achim Rosch, Arkady Krasheninnikov, Hannu-Pekka Komsa, Borna Pielić, Marko Kralj, Martin Hell, Nils Ehlen, Boris Senkovskiy, Alex Grüneis, José Márquez-Velasco, Luca Petaccia, and Giovanni di Santo, as well as financial support through CRC1238 within projects A01 and B06 of DFG are gratefully acknowledged.



- J. Hall, B. Pielić, C. Murray, W. Jolie, T. Wekking, C. Busse, M. Kralj, and T. Michely, 2D Mater. 5 (2018) 025005.
- [2] H. Liu, L. Jiao, F. Yang, Y. Cai, X. Wu, W. Ho, C. Gao, J. Jia, N. Wang, H. Fan, W. Yao, and M. Xie, Phys. Rev. Lett. 113 (2014) 066105.
- [3] S. Barja, S. Wickenburg, Z.-f. Liu, Y. Zhang, H. Ryu, M. M. Ugeda, Z. Hussain, Z.-X. Shen, S.-k. Mo, E.Wong, M. B. Salmeron, F. Wang, M. F. Crommie, D. F. Ogletree, J. B. Neaton, and A. Weber-Bargioni. Nat. Phys. 12 (2016) 751.
- [4] Y. Ma, H. C. Diaz, J. Avila, C. Chen, V. Kalappattil, R. Das, M.-H. Phan, T. Cadez, J. M. P. Carmelo, M. C. Asensio, and M. Batzill, Nat. Commun. 8 (2017) 14231.

Electronic properties of defects in single-layer MoSe₂

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Intrinsic properties of 2D transition metal dichalcogenide semiconductors are highly sensitive to the presence of defects in the crystal structure, due to the confined nature of the electronic wavefunctions. Understanding the defect electronic structure at the atomic scale will enable unprecedented control over material functionality. In this talk I will present two different examples of structural defects in single layers of MoSe₂. Using 4K scanning tunneling microscopy and spectroscopy, and non-contact atomic force microscopy we visualize and directly correlate in 2D MoSe₂ the morphology and electronic properties of structural defects with atomic resolution.

In the first example, we identified linear defects in from of mirror twin boundaries in MoSe₂, which form 1D metal channels embedded in the surrounding semiconductor. At low temperatures these 1D metallic states open a band gap at the Fermi level of 100 meV together with periodic beatings in the local density of states, both characteristic of charge density waves [1]. In the second example, we suggest that the most abundant defect is an O-passivated Se-vacancy, instead of bare Se vacancy as commonly reported. This atomic defect forms an atomically confined Type I hetero junction with the surrounding pristine MoSe₂ and lacks of any in-gap-states. The presence of in-gap-states will be decisive for the different optoelectronic and catalytic properties of the defect.

References:

[1] S. Barja, et al., Nature Physics, 12, 751, (2016)





Fig 1. (a) dI/dV conductance map around the Fermi level, STM image at MoSe₂ valence band and nc-AFM image measured along the same mirror twin boundary in MoSe₂. (b) nc-AFM and STM images of the two same atomic size defects, identified as O-passivated Se vacancies placed in the top (left defect) and bottom (right defect) Se-sublattices.

Grain boundary formation in MoTe₂ by excess-Mo incorporation into the lattice

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Mirror twin grain boundaries (MTBs) have been observed to form with high density in MoSe₂ [1] and MoTe₂ [2] films grown by molecular beam epitaxy (MBE). These MTBs have been shown to be metallic, exhibiting Tomonaga Luttinger quantum liquid behavior [3] and to undergo a Peierls like charge density wave transition [3,4]. What is not understood so far, is why these MTBs form in MBE grown films in the first place. Here we demonstrate that triangular MTB loops (see Fig. 1 (a)) can be formed directly in a pristine MoTe₂ or MoSe₂ by incorporation of vapor deposited atomic molybdenum. Increasing deposition of Mo results in dense networks of MTBs (see Fig. 1(c)). In MoTe₂ over 10% of excess Mo can be incorporated into the Mo-rich MTBs. Using density functional theory (DFT) we show that the formation of these MTBs are energetically favored over Mo-clusters at the surface or individual Mo-interstitials. This observations imply that the same mechanisms are responsible for the high MTB density in MBE grown films.

References:

- Ma, Y.; Kolekar, S.; Coy Diaz, H.; Aprojanz, J.; Miccoli, I.; Tegenkamp, C.; Batzill, M. ACS Nano 2017, 11, 5130-5139.
- [2] Coy Diaz, H.; Ma, Y.; Chaghi, R.; Batzill, M. Appl. Phys. Lett. 2016, 108, 191606
- [3] Ma, Y.; Coy Diaz, H.; Avila, J.; Chen, C.; Kalappattil, V.; Das, R.; Phan, M.-H.; Cadez, T.; Carmelo, J. M. P.; Asensio, M. C.; Batzill, M. Nat. Commun. 2017, 8, 14231.
- [4] Barja, S.; Wickenburg, S.; Liu, Z.-F.; Zhang, Y.; Ryu, H.; Ugeda, M. M.; Hussain, Z.; Shen, Z.-X.; Mo, S.-K.; Wong, E.; Salmeron, M. B.; Wang, F.; Crommie, M. F.; Ogletree, D. F.; Neaton, J. B.; Weber-Bargioni, A. Nat. Phys. 2016, 12, 751.



Fig 1. Formation of mirror twin grain boundary (MTB) loops in $MoTe_2$ by deposition of Mo on a $MoTe_2$ single crystal. (a) STM image of large triangular MTB loop (with ~50 atoms along the side of the triangle). The double row structure imaged in filled state STM is reproduced by simulated STM of the MTB shown in (b). The formation of MTB networks by Mo-deposition onto the $MoTe_2$ surface is shown in (c) in large scale STM images with increasing Mo-deposition from the left (pristine $MoTe_2$) to the right with close to 10% excess Mo incorporated into the $MoTe_2$ sheet by formation of MTBs.

Twisted graphene layers under heterostrain

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Stacking layered materials is a very powerful method to tailor their optical and electronic properties. The properties not only depend on the choice of materials to be stacked but also on the details of the relative arrangement of the layers. For instance, the rotation between the layers has been used to tune the energy of van Hove singularities in twisted graphene layers [1] or to observe the Hofstadter butterfly pattern in graphene on h- BN [2,3]. An even more impressive demonstration of the possibilities offered by precise tuning of the relative arrangement is the recent observation of correlated insulating and superconducting behaviour in magic angle twisted graphene layers [4,5]. Besides rotation, van der Waals stacking offers another possibility to adjust the relative arrangement of the layers: individual stretching of the layers (socalled heterostrain). In the present contribution we will expose scanning tunnelling measurements exploring this possibility in twisted graphene layers [6]. We will show that uniaxial stretching of one layer by only 0.35% with respect to the other layer can dramatically affect the electronic properties of twisted graphene layers with low rotation angle. The amount of heterostrain is determined by a detailed Fourier analysis [7]. With such a low level of heterostrain, we observe a pronounced peak in the density of states at the Dirac energy which we attribute to the emergence of a flat band similar to that observed at magic angles. The strain-induced modification of the band structure could therefore prove useful for the study of the recently discovered correlated electron physics in carbon materials. More generally heterostrain opens up new possibilities for straintronics with 2D materials.



Fig 1. (a) STM image of rotated graphene layers on SiC (V=-400 mV, i=50 pA). The inset shows a zoom in with atomic features (scale bar 1 nm) (b) Spectroscopy of the twisted graphene layers measure at the blue and red dots I panel (a). The resonances E_0 emmerges from a flat band due to heterostrain.

- [1] G. Li et al. Nature Phys. 6, 109 (2009)
- [2] L. A. Ponomarenko et al. Nature 497, 594 (2013)
- [3] C. R. Dean et al. Nature 497, 598 (2013)
- [4] Y. Cao *et al.* Nature, **556**, 80 (2018)
- [5] Y. Cao et al. Nature 556, 43 (2018)
- [6] L. Huder et al. Phys. Rev. Lett. 120 156405 (2018)
- [7] A. Artaud et al. Sci.Rep. 6, 25670 (2016)

Defects and molecular adsorbates on monolayers of MoS₂ on Au(111)

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Monolayers of transition metal dichalcogenides (TMDCs) have matured to an important class of twodimensional materials. Many of them are semiconductors, which is important for optoelectronic devices, with a strong spin-orbit split bandstructure, which is important for spintronic applications.

Here, we grow monolayers of MoS_2 on a Au(111) surface, following the preparation methods from earlier publications (see, e.g. [1]). Using a combination of scanning tunneling microscopy, atomic force microscopy and density functional theory, we identify a variety of point defects. These are missing sulfur atoms as well as interstitial sites inside the MoS_2 layer. Tunneling spectra on these defects reveal characteristic states, which have already been predicted by DFT calculations in similar systems [2,3]. Moreover, we find defects of several nanometers diameter. We assign them to Au vacancy islands [4] and a Au-Mo alloy at the interface to the Au(111) substrate.

Furthermore, we explore the monolayers of MoS_2 on Au(111) as a substrate for organic molecules. We find that adsorbed molecules exhibit a large set of vibronic states. The line shape of these resonances suggests a prolonged lifetime of the electronic excitations as well as a small electron-phonon coupling in the MoS_2 layer.

- [1] Sorensen, et al., ACS Nano 8, (2014) 6788
- [2] Fuhr, et al., Phys. Rev. Lett. 92, (2004) 026802
- [3] González, et al., Nanotechnology 27, (2016) 105702
- [4] Krane, et al., Nano Lett. 16, (2016) 5163

Mind the substrate: SPM characterisation of point-like defects in single-layer MoS₂ on metallic substrates

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Defects, especially -but not only- chalcogenide vacancies, are frequently present in 2D materials regardless of the growth method. Characterisation of 2D samples and their defects by SPM techniques should take into account the presence of metallic substrates, which might substantially alter the electronic properties of the 2D material. The impact of metal substrates on the electronic properties of pristine single-layer MoS_2 has been addressed by Density Functional Theory (DFT) calculations, showing that the interaction between the metal and the MoS_2 can greatly vary depending on the metal [1]. However, the effect of such substrates on the electronic properties of a defected MoS_2 monolayer and its STM characterization has not been systematically analyzed so far.

We have studied the interaction of several point-like defects in a MoS_2 monolayer with underneath Ir(111) and Au(111) substrates by means of DFT calculations and SPM simulations, revealing a notably different behavior depending on the metallic substrate considered. The hybridization of the S states with those of the Ir(111) substrate induces a shift of ~1 eV of the MoS_2 states towards the valence band and a large broadening of the defect states [2]. For both metals, STM simulations within the Tersoff-Hamann approximation show the S vacancies site at both the top and the bottom (in contact to the substrate) layers as dark depressions, with clearly visible S atoms in the MoS_2 lattice, with a more distorted image in the case of the Ir. The interaction with a gold substrate is much weaker, as confirmed by experimental data [3], leading to sharper defect states, more similar to those found for freestanding MoS_2 .

- [1] W. Chen et al., Nano Letters 13, 509 (2013); C. Gong et al., Nano Letters 14, 1714 (2014)
- [2] I. Delac Marion, D. Capeta, B. Pielic, F. Faraguna, A. Gallardo, P. Pou, B. Biel, N. Vujicic and M. Kralj (submitted)
- [3] N. Krane, Ch. Lotze, P. Pou, B. Biel and K. Franke (in preparation)



Fig 1. Left panel: AFM (a) and STM at -0.1 V (b) images of a S vacancy at the top layer for freestanding MoS_2 . **Right panel:** LDOS of top S atoms close (blue) and far (cyan) of the defect site and STM images at V = -0.1 V for a top S vacancy in epitaxial $MoS_2/Au(111)$ (c) and $MoS_2/Ir(111)$ (d). Inset in d): LDOS of a top S vacancy in freestanding MoS_2 .

Exploring optoelectronic properties of point defects in monolayer WS₂ with atomic resolution

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The advent of transition metal dichalcogenides (TMDs) and other two-dimensional (2D) materials has attracted considerable attention due to unique material properties emerging from their reduced dimensionality. Because of this strong confinement, structural defects greatly modify such properties and have therefore become of increasing interest to the 2D materials community. Particularly the creation of ingap defect states is decisive for their optoelectronic properties and catalytic activity.

Using low-temperature scanning probe microscopy with CO functionalized tips we identified and characterized common point defects in monolayer WS_2 (see Fig. 1).

Contrary to previous reports, we suggest that the most abundant defect is an O substitution at a S site, not a S vacancy, with a distinctively different electronic structure.

In contrast to O decorated S vacancies, a W substitutional defect and pristine S vacancies create distinct defect states within the band gap of WS_2 . Interestingly, both types of point defects exhibit spin-orbit split defect states with a large splitting of 80 meV and 280 meV, respectively. Moreover, we have first results that indicate electron-induced light emission from these defects.

The same sample was also characterized with nano-ARPES and photoluminescence spectroscopy, which shows that thermally grown graphene on SiC constitutes a suitable platform for cross-correlation microscopy of TMD materials (and potentially other van der Waals materials) in both, UHV and ambient conditions.

The atomic-scale characterization allows an unprecedentedly detailed picture on the structure and functionality of point defects in 2D-TMDs.



Fig 1. First row: STM topography of different point defects of CVD-grown monolayer WS_2 on multilayer graphene on SiC. Second row: CO-tip AFM images of the same defects with the unit cell of WS_2 indicated. Third row: Strain map derived from the AFM measurements.

Intrinsic and engineered point defects in two-dimensional 1T'-MoS₂

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Monolayer group VI transition metal dichalcogenides (TMDs) exist in either the semiconducting 2H phase or practically semimetallic 1T' phase. While the stable 2H phase has been extensively investigated due to prospective technological applications in electronics and optoelectronics, the metastable 1T' polymorph has appeared in the spotlight only very recently, largely due to its topological properties. Aim of this talk is to provide an overview on the formation of point defects in 1T'-MoS₂ — a prototypical 1T'-TMD — within two experimentally-relevant situations, namely under thermodynamic equilibrium and under electron beam irradiation.

Based on first-principles calculations, firstly I will address the thermodynamic stability of simple point defects, exploring several configurations of vacancy, adatom and antisite defects in sulfur-rich and molybdenum-rich conditions [1]. All considered defects present lower formation energies in the 1T' phase compared to the 2*H* phase, suggesting that the 1T' polymorph is expected to be more susceptible to lattice imperfections. Next, the response of 1T'-MoS₂ to the electron irradiation will be presented [2]. The range of electron beam energies needed to carry out sample imaging without inducing any radiation damages in the lattice and some guidelines for the controlled introduction of defects in the transmission electron microscope are discussed in the light of our molecular dynamics simulations.

Throughout the talk, I will draw comparisons between local disorder in the 1T' polymorph and the well-studied 2H phase in order to portray a complete picture of the role of defects in the different crystalline phases of two-dimensional transition metal dichalcogenides.

- [1] M. Pizzochero and O. V. Yazyev, Phys. Rev. B 96, 245402 (2017)
- [2] M. Pizzochero and O. V. Yazyev, 2D Mater., in press (2018)

1D defects in 2D materials: a theorist's view

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In my talk, I will present an overview of our theoretical efforts aiming at understanding one-dimensional (1D) defects in two-dimensional (2D) materials with a particular emphasis on their atomic structure and electronic transport properties. In single-layer graphene, the relevant 1D defects are the grain boundaries – intrinsic topological defects of polycrystalline materials. We have shown that in graphene low-energy configurations of grain boundaries can be constructed from only two elementary disclinations – pentagons and heptagons [1,2], while small-angle grain boundaries are dramatically stabilized by the out-of-plane deformation, a remarkable feature of graphene as a 2D system [1,3]. Regular grain boundaries in graphene are predicted to exhibit two distinct transport behaviors - either perfect reflection or high transparency with respect to low-energy charge carriers [4]. It is also shown that certain periodic line defect structures can be engineered and offer opportunities for generating valley-polarized charge carriers [5]. In multilayer graphene systems, the stacking order degree of freedom gives rise to stacking domain boundary defects. I will introduce a theoretical model that explains the emergence of the lattice of stacking domain boundaries in low-angle twisted bilayer graphene [6] and discuss the intriguing transport properties of such defects observed in experiments [7]. Two-dimensional transition metal dichalcogenides (TMDs) display a much richer diversity of 1D imperfections thanks to their binary composition and structural polymorphism [8]. I will discuss the possibility of spin-filtering of charge-carriers upon transmission across inversion domain boundaries in single-layer H-phase TMDs [9] and the topological states at the 1H/1T interfaces of WSe₂ that were recently observed in experiments [10].

- [1] O. V. Yazyev and S. G. Louie, Phys. Rev. B 81, 195420 (2010).
- [2] O. V. Yazyev and Y. P. Chen, Nat. Nanotechnol. 9, 755 (2014).
- [3] Y. Tison, J. Lagoute, V. Repain, C. Chacon, Y. Girard, F. Joucken, R. Sporken, F. Gargiulo, O. V. Yazyev and S. Rousset, Nano Lett. **14**, 6382 (2014).
- [4] O. V. Yazyev and S. G. Louie, Nat. Mater. 9, 806 (2010).
- [5] J. H. Chen et al., Phys. Rev. B 89, 121407(R) (2014).
- [6] F. Gargiulo and O. V. Yazyev, 2D Mater. 5, 015019 (2018).
- [7] M. M. Benameur, F. Gargiulo, S. Manzeli, G. Autes, M. Tosun, O. V. Yazyev and A. Kis, Nat. Commun. 6: 8582 (2015).
- [8] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev and A. Kis, Nat. Rev. Mater. 2, 17033 (2017).
- [9] A. Pulkin and O. V. Yazyev, Phys. Rev. B 93, 041419(R) (2016).
- [10] M. M. Ugeda et al., arXiv:1802.01339.

Polariton Hall Effect in Transition-Metal Dichalcogenides

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We analyze the properties of strongly coupled excitons and photons in systems made of semiconducting two-dimensional transition-metal dichalcogenides embedded in optical cavities. Through a detailed microscopic analysis of the coupling we unveil novel, highly tunable features of the spectrum, that result in polariton splitting and a breaking of light-matter selection rules. The dynamics of the composite polaritons is influenced by the Berry phase arising both from their constituents and from the confinement-enhanced coupling. We find that light-matter coupling emerges as a mechanism that enhances the Berry phase of polaritons well beyond that of its elementary constituents, paving the way to achieve a polariton Hall effect.

References:

[1] arXiv: 1802.02527



Fig 1. (a) Art illustration of the generation and STM analysis of individual vacancies in graphene layers. (bc) 4K STM data showing atomically resolved images of C vacancies in graphene layers growth of graphite and Pt(111) and its impact in the electronic density of states of the graphene layers.

Realization of Single Atom Magnets through 2D Decoupling Layers

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Single atom magnets are the smallest possible magnetic storage unit. After almost two decades of search, they were discovered only 2 years ago [1,2]. 2D decoupling layers are essential in their realization since all magnetic atoms adsorbed directly onto metal surfaces are paramagnetic, *i.e.*, their magnetization curves are fully reversible and display no magnetic remanence, even in cases of the largest possible large magnetic anisotropy [3]. We begin to understand what stabilizes the magnetic quantum states on decoupling layers. Three ingredients are needed. The symmetry of the adsorption site determines which magnetic states contribute to the ground state wave function and under which conditions magnetization reversal by tunneling is possible. Excitations by electrons and phonons can lift the system into states from where reversal is possible. Therefore, both have to be avoided, and this is the role played by the decoupling layer. It has to have low phonon and electronic density of states in the energy range of interest.

For Dy atoms, the conditions of stable magnetization are met on graphene on Ir(111) [2]. Since graphene forms a moiré pattern on Ir(111), the atoms are also steered to equidistant sites, see left hand side of the Figure below. Similar to molecular magnets, the magnetization curves of Dy/g exhibit steps when magnetic levels cross. They occur at \pm 2.7 T and \pm 5.6 T, and the magnetic remanence is 30 % of the saturation magnetization at 2.5 K, see right hand side of Figure below. Ho atoms on two monolayer thick MgO(100) films grown on Ag(100) where found to exhibit magnetic remanence up to 30 K and magnetic relaxation times of at least one hour at 2 K [1]. This result was obtained from ensemble measurements using X-ray magnetic circular dichroism (XMCD). Spin-polarized scanning tunneling microscopy (STM) measurements demonstrated reading and writing of individual Ho atoms and confirmed their long magnetic lifetimes [4]. Very recent STM experiments show stable magnetization over two hours in external fields of 8 T that are applied opposite to the magnetization of the atoms and at temperatures of 35 K; the first spontaneous switching from the metastable to the field-stabilized state is observed at 45 K [5]. The combined coercitive field, remanent magnetization, and thermal stability of Ho/MgO(100) outperforms the best single molecular magnets that exhibit remanence up to 60 K, but only 1 % of the saturation [6]. Recently, electron paramagnetic resonance (ESR) has been realized on individual Fe atoms with the STM [7]. This gives access to the coherence time of the magnetic states, which is one of the benchmarks of qubits. We will elaborate on the possibility of single atom qubits.

References:

- [1] F. Donati et al., Science 352, 318 (2016)
- [2] R. Baltic et al., Nanolett. 16, 7610 (2016)
- [3] I. G. Rau *et al.*, Science **344**, 988 (2014)
- [4] F. D. Natterer *et al*. Nature **543**, 226 (2017)
- [5] F. D. Natterer, F. Donati, F. Patthey and H. Brune, arXiv:1712.07871, PRL submitted (2018)
- [6] C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton, and D. P. Mills, Nature 548, 439 (2017)
- [7] S. Baumann, W. Paul, T. Choi, C. P. Lutz, A. Ardavan, and A. J. Heinrich, Science 350, 417 (2015)



Left: STM image of Dy atoms on g/Ir(111); **right**: M(H)-curve showing remanent magnetization at 2.5 K [2].

A closer look at electrochemically transferred 2D materials

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Macroscopic domains of single-layer h-BN and graphene can be grown by low-pressure CVD on singlecrystalline metal substrates under UHV conditions [1]. For most foreseeable applications these single-layer materials need to be delaminated from their metallic growth templates and transferred to other supports. Electrochemical treatment, inducing mechanical delamination by the formation of hydrogen bubbles [2,3], has been applied successfully for separating graphene layers from metal substrates. A two-step electrochemical process, involving the interaction of the monolayer with tetraoctylammonia ions before the bubbling step, has been shown to enable quantitative transfer of graphene [4,5] and h-BN [6] monolayers from single-crystal metal surfaces, preserving the single-domain character over large scales. This talk will present post-transfer analyses of such single layers using various surface science methods.

References:

- [1] M. Corso et al., Science 303, 217 (2004).
- [2] L. Gao et al., Nature Commun. 3, 699 (2012).
- [3] E. Koren et al., Appl. Phys. Lett. 103, 121602 (2013).
- [4] L. Koefoed et al., J. Phys. D Appl. Phys. 48, 115306 (2015).
- [5] E. Miniussi et al., J. Phys.: Condens. Matter 29, 475001 (2017).
- [6] H. Cun et al,. Nano Letters 18, 1205 (2018).



Fig 1. (a) STM image (95 nm x 95 nm) of h-BN/Rh(111) nanomesh with intentionally created 2 nm voids ($V_t = -1.0 V$; $I_t = 0.5 nA$); (b) STM image (76 nm x 76 nm) of the same h-BN monolayer after electrochemical delamination, transfer onto Rh(111) under ambient condition, and subsequent annealing in UHV.

Atomically thin films of Na₃Bi: A platform for topological electronics

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The semiconductor industry recognizes a need for a new computing technology with vastly lower energy consumed per operation than silicon CMOS. The discovery in the last decade of topological phases of matter offers a new route to low-energy switches based on the conventional-to-topological quantum phase transition (QPT). Here we investigate ultra-thin films of topological Dirac semimetal (TDS) Na₃Bi as a candidate material for an electric-field tuned QPT.

Na₃Bi thin films are grown by molecular beam epitaxial and transferred in UHV to a low-temperature scanning tunneling microscope (STM) capable of magnetotransport at 5 K. Thin films (20 nm) of Na₃Bi on α -Al₂O₃(0001) substrates are found to possess low temperature charge carrier mobilities exceeding 6000 cm²V⁻¹s⁻¹ with *n*-type carrier densities below 10¹⁸ cm⁻³[1], comparable to single crystal values. Mapping the local Dirac point via scanning tunneling spectroscopy (STS) reveals a high degree of spatial uniformity, with *rms* variations in Dirac point energy less than 5 meV[2], comparable to the best graphene samples on hexagonal boron nitride. Chemical doping[3] and electrostatic gating[4] (using SiO₂/Si substrates) can be used to tune the carrier density, first steps toward a topological transistor. Atomically thin monolayer and bilayer Na₃Bi are shown to be large (>400 meV) bandgap 2D topological insulators using STS and angle-resolved photoemission spectroscopy (ARPES). An electric field applied by varying tip sample separation (STS) or potassium dosing (ARPES) is seen to fully close the bandgap and re-open it as a conventional insulator, a field-tuned quantum phase transition.

References:

- [1] J. Hellerstedt et al., Nano Letters 16, 3210 (2016).
- [2] M.T. Edmonds et al., *Science Advances* **3**, eaao6661 (2017).
- [3] M.T. Edmonds et al., ACS Appl. Mater. Interfaces 8, 16412 (2016).
- [4] J. Hellerstedt et al., PRMaterials 1, 054203 (2017).
- [5] J.L. Collins et al., *submitted*.



Fig 1. (a) STM topograph of ultra-thin epitaxial Na_3Bi on Si(111). (b) Atomic structure of Na_3Bi illustrating monolayer and bilayer units. (c) Individual scanning tunneling spectra of bilayer Na_3Bi at different tip heights (electric fields) as shown in legend. (d) Bandgap as a function of electric field for monolayer and bilayer Na_3Bi .

Probing electrical field tunable bandgap and defects in black phosphorus

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Two-dimensional black phosphorus (BP) has sparked enormous research interest due to its high carrier mobility, layer-dependent direct bandgap and outstanding in-plane anisotropic properties. BP is one of the few two-dimensional materials where it is possible to tune the bandgap over a wide energy range from the visible up to the infrared. Here we demonstrated a giant Stark effect in few-layer BP via electrostatic gating. Using low-temperature scanning tunnelling microscopy (LT-STM), we observed that a monotonic reduction of the bandgap of few layer BP occurs after the injected electrons compensate the existing defect-induced holes. Eventually, we achieved up to 35.5% bandgap modulation in the light-doping regime. When probed by STM spectroscopy, the local density of states in few-layer BP shows characteristic resonance features arising from layer-dependent sub-band structures due to quantum confinement effects. The demonstration of an electrical field tunable bandgap in BP paves the way to designing electro-optic modulators and photodetector devices that can be operated in a wide electromagnetic spectral range. In addition, we also employed LT-STM to probe the charge state of shallow acceptors in black phosphorus together with an aim to understand the spatial structures of bound hole states near individual acceptors. Our findings open up the new avenue for the investigation into charge transport through single dopants in gated BP nanodevices.

References:

[2] Nano Letters 17 (3), 1970-1977, 2017



Fig 1. (a) Schematic illustration of a back-gated few-layer BP device (b) STM imaging of atomic lattice in BP. (c) Field tunable bandgap measured by local STM spectroscopy.

^[1] Nano letters 17 (11), 6935-6940, 2017

Group IV analogs to Graphene

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Here I will review our work on STM studies of UHV-grown group IV 2D materials (graphene, silicene, germanene, stanene). UHV growth on single crystal metals allows us to study pristine surfaces and interfaces, which is particularly important for the Si, Ge, and Sn graphene analogues which can't be exfoliated from bulk. In all of these systems, we find a competition between 2D material growth and surface alloying. In the germanium system, we observe a Cu₂Ge surface alloy with a 4.4Å lattice constant consistent with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction of Cu(111). We also find regions with a triangular lattice with 3.8 Å spacing that we attribute to buckled germanene. The ratio of surface alloy to germanene depends on the growth temperature in a narrow window. Notably, we have observed tip-induced "exfoliation" of bilayer germanene which shows two layers of 3.8 Å lattices indicating a particular stacking arrangement. The gapped dirac cone band structure expected for germanene was not observed in tunneling spectroscopy, which we attribute to coupling between the germanene and Cu(111) states. In the tin system we observe two types of surface alloy: CuSn, a 5.2 Å lattice that corresponds to the 2x2 reconstruction of the Cu(111) surface, and Cu₂Sn, a 4.4 Å lattice that is commensurate with the ($\sqrt{3} \times \sqrt{3}$) reconstruction of Cu(111). We also observe nanoscale regions with a 4.67 Å lattice which is close to predictions for free standing stanene.[1] As in the germanene case, tunneling spectroscopy does not show the expected gapped Dirac density of states. We perform DFT calculations that confirm the stability of these surface alloys and provide insight into the competition between surface alloying and 2D material growth. To minimize surface alloying and decouple the 2D material from the substrate, we are currently working towards UHV growth of an intervening hexagonal boron nitride (hBN) buffer layer. By depositing ammonia borane complex, then heating the copper substrate to ~900C we are able to form smooth, flat areas of hBN that originate at the copper step edges and grow laterally onto the terraces. Future work will determine if in-situ grown hBN will sufficiently decouple the stanene and germanene states from the underlying copper states.

References:



Fig 1. 5K STM topographs. (ab)monolayer graphene on Cu(111) shows continuous growth over step edges (a) and some point defects attributed to vacancies (b). (c) 3.8Å lattice, likely monolayer germanene on Cu(111). (d). 4.4Å lattice consistent with a Cu₂Ge surface alloy. (e). 5.2Å lattice (yellow shading) consistent with CuSn surface alloy and 4.67Å lattice (blue shading) indicating buckled stanene.

Programmable Doping of a Two-Dimensional van der Waals Semiconductor with Atomic Scale Imaging and Spectroscopy

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We report new device architectures of two-dimensional (2D) integrated circuits (ICs), where atomically thin circuit components are seamlessly integrated within the single atomic-planes. The first type was achieved by coplanar heteroepitaxy of 2D transition-metal dichalcogenide (TMDC) polymorphs, [1-3] where the distinct metallic and semiconducting atomic layer crystals were stitched by a sequential chemical vapor deposition. It was verified that these coplanar metal-semiconductor contacts are atomically coherent, showing the lowest contact barrier height ever-reported, which immediately contributed to the substantial outperformance of the coplanar field-effect transistors (FETs) over conventional top-contact 2D TMDC FETs. The second one was realized by exploiting a novel concept of light-induced doping of a TMDC semiconductor film with a scanning light probe, [4-6] with which both n- and p-doped channels were selfassembled to form lateral p-n junctions [7]. Therein, we provide direct evidence of a microscopic doping mechanism by atomic scale imaging and spectroscopy. This real-time writing process is precisely controllable within a minute, in that diffusive doping profiles can be controlled at the sub-micrometer scale, and doping concentrations are tunable to vary the channel sheet resistance over five orders of magnitudes. As such, we assembled both n- and p-doped channels within the same atomic planes to fabricate 2D device arrays of n-p-n (p-n-p) bipolar junction transistor amplifiers and radial p-n photovoltaic cells in high performances. This doping method can be potentially used to fabricate designer 2D circuits based on atomically thin semiconductors in arbitrary shapes.

- [1] Ji-Hoon Ahn et al., Nano Lett., 15, 3703 (2015)
- [2] Ji Ho Sung et al., Nature Nanotechnol., 12, 1064, (2017)
- [3] Hoseok Heo et al., Nature Comm. 6, 7372 (2015)
- [4] Kanghyun Chu et al., Nature Nanotechnol., 10, 972 (2015)
- [5] Myoung-Jae Lee et al., Nature Comm., 7, 12011 (2016)
- [6] Soonyoung Cha et al., Nature Comm., 7, 10768 (2016)
- [7] Seung-Young Seo et al., Submitted (2018)

POSTERS

Controllable Switching of the Superconductivity of a Tungsten STM Tip on Epitaxial Graphene

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Epitaxial Graphene on metals has become a playground for a wide range of 2D systems displaying competing interactions that may lead to long range magnetic order, Kondo resonances or superconductivity [1], with STM as a favorite tool to probe their LDOS at the atomic level.

We present a systematic study of a controllable functionalization of tungsten tips on gr/Ir(111) and gr/Pb/Ir(111) that produces superconducting (SC) tips. Starting from Ar+ sputtered pristine tungsten tips, we reproducibly build a SC nanostructure at the tip apex by means of voltage pulses on several graphene-covered surfaces (see Figure 1(a)). We have further tested these SC tips on a Cu(111) surface, finding that the copper surface state and the tip SC gap can be resolved simultaneously in the STS spectra. The superconductivity of the tip can be switched off by tip manipulation on clean metallic substrates.

We have characterized the resulting SC gap as a function of temperature (see Figure 1(b)) and magnetic field, obtaining a transition temperature close to 3.7 K and a critical field well above 3T in all cases. This suggests the formation of a tungsten-based amorphous nanocarbon compound at the tip, in agreement with the known fact that superconductivity can be present in tungsten carbide bulk alloys [2] and nanostructures [3].

The present result should be taken into account when studying zero-bias features like Kondo or superconductivity by means of STM, especially when using tungsten tips on carbon-based surfaces or 2D systems.

References:

- [1] M. Garnica et al, Nature Physics, 9, 360 (2013)
- [2] R.H. Willens and E. Buehler, Appl. Phys. Lett. 7, 25 (1965)
- [3] I. Guillamón et al, New Journal of Physics 10, 093005 (2008)



Figure 1: (a) STS spectrum recorded at 1.1 K on gr/Pb/Ir(111) with a functionalized superconducting tungsten carbide tip. (b) Temperature evolution of the superconducting gap.

First-principles study of ultrasensitive H₂S gas sensors based on p-type WS₂ hybrid materials

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Gases with different properties, origins, and concentrations are pervasive in our environment. Some of these gases are highly toxic and hazardous, while others are essential for life or indicators of health status. Accordingly, sensors for gas detection and monitoring are needed in various sectors such as environmental protection, industrial process monitoring and safety, amenity, energy saving, health, and food industries. [1] Metal oxide semiconductors stand out as the most common active sensing materials used in practical devices. Among the new types of nanoscopic sensors being studied, layered transition metal dichalcogenide (MX_2 , M = Mo, W; X = S, Se) nanostructures have recently attracted significant interest. Often compared to graphene and other two-dimensional (2D) nanomaterials, their properties present distinct advantages for electronic, optical, and electrochemical sensors. [2]

In this contribution, we explore the gas sensing behaviour of WS₂ nanowire-nanoflake hybrid materials and demonstrate their excellent sensitivity (0.043 ppm⁻¹) as well as high selectivity towards H₂S relative to CO, NH₃, H₂, and NO (with corresponding sensitivities of 0.002, 0.0074, 0.0002, and 0.0046 ppm⁻¹, respectively). Gas response measurements, complemented with the results of X-ray photoelectron spectroscopy analysis and first-principles calculations based on density functional theory, suggest that the intrinsic electronic properties of pristine WS₂ alone are not sufficient to explain the observed high sensitivity towards H₂S. A major role in this behaviour is also played by O doping in the S sites of the WS₂ lattice. The results of the present study open up new avenues for the use of transition metal disulphide nanomaterials as effective alternatives to metal oxides in future applications for industrial process control, security, and health and environmental safety. [3]

- [1] Neri, G. Chemosensors 2015, 3, 1-20
- [2] Li, B. L.; Wang, J. P.; Zou, H. L.; Garaj, S.; Lim, C. T.; Xie, J. P.; Li, N. B.; Leong, D. T. Adv. Funct. Mater. 2016, 26, 7034–7056.
- [3] Asres, G. A.; Baldoví, J. J.; Dombovari, A.; Järvinen, T.; Lorite, G. S.; Mohl, M.; Shschukarev, A.; Pérez Paz, A.; Xian, L.; Mikkola, J.-P.; Spetz, A. L.; Jantunen, H.; Rubio, A.; Kordas, K. Nano Research, 2018, DOI: https://doi.org/10.1007/s12274-018-2009-9

Confinement of iridium surface state below hydrogenated graphene.

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A continuous layer of graphene grown on metallic substrates such as Ir(111) has been found to protect metallic 2D surface state even at ambient conditions.[1] For the graphene nano-island the interaction with the substrate at the edges restricts the appearance of the surface state into a small region that is rigorously determined by the profile of the island.[2] The size and shape of islands are typically not possible to prepare in a well-defined manner due to a stochastic nature of the growth process. Here, we use a continuous layer of graphene and introduce strong scattering centers to iridium surface state by creating covalent bonds between the graphene and iridium using hydrogen functionalization. By employing hydrogenation at high temperature we create a triangular periodic pattern of scattering centers with 25A periodicity. [3] For the perfect H-pattern we observe no surface state under graphene. However, by removing single H-cluster, a surface state confined into a small region bound by neighboring H-clusters can be observed. Desorption of hydrogen clusters with STM tip allows lateral manipulation of the iridium surface state in a controlled manner.

References:

- [1] Varykhalov, et.al., PRL, 108(6), 066804
- [2] Hämäläinen, et.al., PRL, 107(23), 236803 and Jolie, et.al, PRB, 89(15), 155435-6
- [3] Jørgensen, et.al., ACS Nano, 10(12), 10798-10807



Fig 1. (a) Topography and (b) dI/dV map of graphene on Ir(111) hydrogenated at high temperature. The missing hydrogen cluster is marked by a dashed circle. The dI/dV map at -400meV resolves a surface state of iridium confined into a small circular region with 4nm diameter (c).

Exploring the optical and electronic properties of new layered material TiS₃: Combining experimental and theoretical methods

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The isolation of graphene and transition metal dichalcongenides has opened a veritable world to a great number of layered materials which can be exfoliated, manipulated, and stacked or combined at will. Here, we present the properties of the transition metal trichalcogenide (TMTC) **TiS**₃, as a novel material for next generation electronics and optoelectronics [1]. TiS₃ nanosheets have proven to be promising candidates for ultrathin optoelectronic devices due to their direct narrow band-gap and their strong light-matter interaction [2]. In addition, the marked in-plane anisotropy of TiS₃ can result in novel devices sensitive to the light polarization [3]. In this poster, a complete study of the electronic and optical properties combining experimental and theoretical methods is presented for TiS₃.

One the one hand, scanning tunneling spectroscopy and photoelectrochemical measurements are combined with RPA and BSE calculations to obtain the electronic and optical bandgaps and thus the exciton binding energy. The exciton binding energy is orders of magnitude larger than that of common semiconductors and comparable to bulk transition metal dichalcogenides, making TiS_3 ribbons a highly interesting material for optoelectronic applications and for studying excitonic phenomena even at room temperature [4]. Furthermore, we demonstrate how the band gap can be modified by inducing tensile or compressive strain. The ability to control the bandgap and its nature can have a wide impact in the use of TiS_3 for optical applications. [5]

On the other hand, we study the optical contrast of TiS_3 nanosheets, from which we obtain the complex refractive index in the visible spectrum. Using both unpolarized and linearly polarized light we find that TiS_3 exhibits very large birefringence, larger than that of well-known strong birefringent materials like TiO_2 or calcite, and linear dichroism. These findings are in qualitative agreement with *ab-initio* calculations that suggest an excitonic origin for the birefringence and linear dichroism of the material. [6]

- [1] J. O. Island, A. J. Molina-Mendoza, M. Barawi, R. Biele, J. M. Clamagirand, J. R. Ares, C. Sanchez, H. S. J. van der Zant, R. D'Agosta, I. J. Ferrer, and A. Castellano-Gomez, *2D Materials*, **4**, 022003 (2017)
- [2] J. O. Island, M. Barawi, R. Biele, A. Almazán, J. M. Clamagirand, J. R. Ares, C. Sánchez, G. A. Steele, H. S. J. van der Zant, J. V. Alvarez, R. D'Agosta, I. J. Ferrer, and A. Castellanos-Gomez, *Advanced Materials* 27, 2595 (2015)
- [3] J. O. Island, R. Biele, M. Barawi, J. M. Clamagirand, J. R. Ares, C. Sánchez, H. S. J. van der Zant, I. J. Ferrer, R. D'Agosta, and A. Castellanos-Gomez, *Scientific Reports* 6, 22214 (2016)
- [4] A. J. Molina-Mendoza, M. Barawi, R. Biele, E. Flores, J. R. Ares, C. Sánchez, G. Rubio-Bollinger, N. Agraït, R. D'Agosta, I. J. Ferrer, and A. Castellanos-Gomez, *Advanced Electronic Materials* 1, 9 (2015)
- [5] R. Biele, E. Flores, J. R. Ares, C. Sanchez, I. J. Ferrer, G. Rubio-Bollinger, A. Castellanos-Gomez, and R. D'Agosta, *Nano Research* (2018), **11**, pp 225–232
- [6] N. Papadopoulos, R. Frisenda, R. Biele, E. Flores, P. Gant, J. R. Ares, C. Sanchez, G. A. Steele, H. S. J. van der Zant, I. J. Ferrer, R. D'Agosta, and A. Castellanos-Gomez, "Birefringence and linear dichroism of TiS₃ nanosheets", *submitted (2018)*
The many faces of the topological insulator BiTeCl

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Owing to its inversion asymmetry, strong polarization and spin-orbit coupling (SOC), BiTeCl is a candidate spintronic compound [1-3] and a reported inversion asymmetric topological insulator (IATI) [4]. Furthermore, the accidental presence of a Bi2TeCl crystal structure, a predicted weak topological insulator (WTI) [5], and exposed quasi 2D Bi bi-layers [6], provide for a rich environment for studying exotic topological phenomena.

We investigate the surface terminations and electronic properties of BiTeCl, a tri-layered, non-centro symmetric, polar semi-conductor, who's band-gap width is being under discussion in the scientific community. We contest, by means of Scanning Tunneling Microscopy/Spectroscopy (STM/S) experiments, several key points including, termination dependent electronic structures as the origin of the band gap inconsistencies and the highly contested issue of the presence or lack of a non-trivial topological state. We therefore discuss these aforementioned inconsistencies, alongside presenting entirely new structures, defects and evidence of sub-band structure.

References:

- [1] K. Ishizaka et al., Nature Materials 10, 521–526 (2011)
- [2] A. Crepaldi et al., Phys. Rev. Lett. 109, 096803
- [3] Y. Kohsaka et al., Phys. Rev. B 91, 245312
- [4] Y. L. Chen et al., Nature Physics 9, 704–708 (2013)
- [5] P. Tang et al., Phys. Rev. B 89, 041409(R)
- [6] I.K.Drozdov et al., Nature Physics 10, 664–669 (2014)
- [7] Y. J. Yan et al. Journal of Physics:Condensed Matter Vol. 27, (47)



Fig 1. STM images of the three most common surface terminations of BiTeCl.

Electronic structure of Pb islands on graphene: hints for a weak interface coupling

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One of the notable features of graphene is its chemical inertness. While being an advantage in many respects, this property hinders the introduction in graphene of new electronic phases, such as ferromagnetism and superconductivity. By means of low temperature scanning tunneling microscopy (STM) and ab-initio calculations we study the electronic structure of crystalline Pb islands, a prototypical superconductor, grown on the graphitized SiC(C face). Their electronic structure, dominated by quantum well states [1], is found to be very close to the band structure of freestanding Pb(111) films as computed by ab-initio calculations. Furthermore, differential tunneling conductance on the islands shows the signature of dynamical Coulomb blockade [2]. On the graphene's side, there is no evidence of electron scattering at the interface with lead. Our findings indicate a week mechanical and electronic coupling between the graphene and the deposited lead film.

- [1] T.-C. Chiang Surf. Sci. Rep. 39 181 (2000)
- [2] C. Brun et al., Phys. Rev. Lett. 108 126802 (2012)



Fig 1. (a) Topographic STM image showing Pb islands grown on the surface of multilayer graphene on SiC. (b) STS spectrum measured at 8.5K in the center of a 14 ML Pb island. Rectangular-shaped features comes from the M-shaped bands near the Brillouin zone center. The inset shows the signature of the dynamical Coulomb blockade on the spectra in vicinity of the Fermi level on three islands of different area. (c) Calculated band structure of a freestanding 14 ML Pb(111) film. One of the M-shaped bands is highlighted with blue.

Mapping the spin distribution in surface-confined lanthanide derivatives by the Kondo effect

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The magnetic properties of organic 2D materials are a fertile ground to explore the competition of quantum fluctuations and long range order. The scattering from a single magnetic impurity by spin flip results in the appearance of a sharp Kondo resonance at the Fermi level that can be detected by STS.¹

Fluorinated porphyrins (2H-4FTPP) were deposited on Au(111) under UHV. They do not have magnetic moment and were metallated in-situ by a lanthanide archetype (Dy), affording the expression of Dy-2H-4FTPP, Dy-1H-4FTPP and Dy-0H-4FTPP species. Importantly, such Dy derivatives could be deprotonated selectively in the step by step fashion Dy-2H-4FTPP --> Dy-1H-4FTPP --> Dy-0H-4FTPP by vertical manipulation with the tip of the STM. A Kondo resonance is observed for Dy-2H-4FTPP or Dy-0H-4FTPP, thus an unprecedented irreversible Kondo switch off through control of coordination bonding was illustrated. By tracking the width of the Kondo resonance of the Dy-2H-4FTPP species as a function of the temperature,² a Kondo temperature of 120 K was found. Unexpectedly for a lanthanide containing molecule,³ the intensity of the Kondo resonance is optimal problems of the molecule, being absent on the lanthanide center.

In summary, the capability of lanthanide elements to afford the expression of Kondo phenomenon while embedded in surface-confined macrocycle environments, as well as its tunability by tip-induced electric stimuli is presented, thus opening new ways for designing and tailoring Kondo systems on surfaces.

- [1] V. Madhavan et al. Science 280, 567, 1998
- [2] M. Ternes. J. Phys. Condens. Matter 21, 053001, 2009
- [3] K. Katoh et al. Dalton Trans., 39, 4708, 2010.



Fig 1. Left panel) Kondo Spectrum of Dy-2H-4FTPP (black line) and Dy-1H-4FTPP (blue line) species on Au(111) recorded at 4.4 K. The Zero Bias Resonance spectrum has been fitted to the Fano resonance expression (red empty dots). The spectrum recorded on top of the Dy-1H-4FTPP species (blue) shows no sign of the Kondo resonance. The inset displays a tentative scheme of the conformation of Dy-2H-4FTPP species. Right panel) Spatial distribution of the Kondo resonance in the Dy-2H-4FTPP Species on Au(111). A 3D representation of a STM topograph (bottom) superimposed by slices of constant energy LDOS maps. The successively stacked slices of constant energy LDOS maps are extracted from a CITS map at the selected energies.

Electric Field-Tuned Topological Phase Transition in Ultra-Thin Na₃Bi – Towards a Topological Transistor

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The electric field induced quantum phase transition from topological to conventional insulator has been proposed as the basis of a topological field effect transistor. In such a device an electric field can switch 'on' the ballistic flow of charge and spin along dissipationless edges of the two-dimensional (2D) quantum spin Hall insulator [1], and when 'off' is a conventional insulator with no conductive channels. Here we demonstrate that few-layer Na₃Bi, normally a 3D Topological Dirac semimetal in its bulk[2][3], is a viable platform for realising such a topological transistor at room temperature.

Using scanning tunnelling microscopy (STM)/spectroscopy (STS), supported by complementary angleresolved photoelectron spectroscopy (ARPES), we observe that mono- and bilayer Na₃Bi behave as effectively 2D topological insulators with bulk bandgaps >400meV. Further, we demonstrate that upon the application of an external electric field [4] with an STM tip, a topological phase transition to trivial insulator with conventional gap greater than 100meV can be reversibly induced. The large bandgaps in both the conventional and quantum spin Hall phases suggest that Na₃Bi is suitable for room temperature topological transistor operation.

- [1] C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 226801 (2005)
- [2] Liu, Z. K. et al. Science 343, 6173, pp. 864–867 (2014)
- [3] C. Niu, et al., Phys. Rev. B 95, 075404 (2017)
- [4] Pan, H., Wu, M., Liu, Y. & Yang, S. A. Sci. Rep. 5, 1–10 (2015)

Electronic consequences of chemical doping of 7-Armchair Graphene Nanoribbons

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The tunable electronic structure of Graphene Nanoribbons (GNRs) with different edge types has provoked great interest due to potential applications in electronic devices as molecular diodes or transistors. Thanks to the on-surface synthesis of chemically customized molecular precursors, nanoribbons with atomically defined structure can be grown [1]. This high precision in their bottom-up growth allows to tune their electronic structure via width control or chemical doping. Here we use two different strategies to chemically modify 7-armchair GNRs (7-AGNRs) to clarify how the chemical modifications on the nanoribbons' structure affect their electronic properties. By means of Scanning Tunneling Spectroscopy we tackle with atomic precision this issue on 7-AGNRs with substitutional nitrile functional groups at the ribbons' edges and on 7-AGNRs with substitutional boron atoms within the ribbons' backbone. We find that in the first case the CN groups lead to an efficient n-like doping of the ribbon [2], while in the second case B atoms induce the formation of a new acceptor band and bandgap renormalization.

- [1] L. Talirz; P Ruffieux; R Fasel. Advanced materials 28, 6222 (2016)
- [2] E. Carbonell Sanromá; J. Hieulle; M. Vilas Varela; P. Brandimarte; M. Iraola; A. Barragán; J. Li; M. Abadia; M. Corso; D. Sánchez Portal; D. Peña; J. I. Pascual. ACS Nano 11, 7355, 2017

Mapping Local Resistance of Sidewall Graphene Nanoribbons

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Epitaxial graphene on SiC represents one of the most promising candidates for large-scale integration of graphene-based electronics. In particular, epitaxial graphene sidewall nanoribbons (GNRs) are nanostructures of fundamental interest which can provide direct and controllable access to charge neutral graphene [1]. High-temperature epitaxial growth methods can provide exceptionally homogeneous and pure GNRs samples [2]. Due to quantum confinement effects, exceptional ballistic transport at room temperature was recently observed in these systems [3]. Ballistic transport in graphene close to the Dirac point has been the subject of several theoretical studies, but its fundamental aspects are not yet fully understood.

Using a cryogenic combined AFM/STM setup, we measure the local resistance and potential of GNRbased devices with nm-scale spatial resolution and μ V-scale voltage resolution. Local potential and resistance, measured at room temperature both in the invasive and non-invasive probe regimes, show plateaus and nonconstant slopes which provide clear indication of non-diffusive transport.

References:

- [1] Palacio et al., Nano Lett. 15 (1), pp. 182–189 (2014)
- [2] Sprinkle et al., Nature Nanotechnology 5, pp. 727–731 (2010)
- [3] Baringhaus et al., Nature 506, pp. 349–354 (2014)



Fig 1. (left) Schematic representation of a sidewall GNR between two metallic contacts explored by a scanning probe tip. (right) Local resistance to nearest contact as a function of distance showing plateaus and varying slopes.

Coexistence of distinct 3x3 structural distortions in the charge density wave state in NbSe₂

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NbSe₂ is a prototypical layered material with a rich electronic phase diagram that includes a charge density wave (CDW) phase transition at low temperatures ($T_c = 33$ K). This CDW phase transition simultaneously triggers a modulation of the electronic density with a quasi-commensurate 3x3 order and an in-plane elastic distortion of the Nb lattice. Despite the CDW state has been intensively studied in this material, not much is yet known about how the atomic rearrangement in the Nb lattice occurs leading to the 3x3 electronic modulation. In this work we address this question by combining density functional theory (DFT) calculations with low-temperature (T = 1 K) scanning tunneling microscopy (STM) imaging. Our DFT calculations show that the 3x3 electronic modulation in NbSe₂ can be induced by different structural rearrangements in the Nb plane. These calculated structural phases result very close in energy within few meVs, which makes feasible their coexistence at finite low temperatures. Our STM measurements in bulk and single-layer NbSe₂ confirm the coexistence of at least two of the calculated phases. These phases are identified by comparing the experimental STM images with the calculated ones for both empty and occupied states. Lastly, we show that switching between these two CDW phases can be achieved via the bias voltage.



Fig 1. Atomically resolved STM image acquired in bulk 2H-NbSe₂ showing the coexistence of two 3x3 lattice distortions induced by the CDW state at 1 K.

Development of a true variable temperature gateble-STM/AFM in ultra high vacuum conditions to probe 2D materials

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Since their first isolation, 2D materials have been widely studied, showing very interesting properties, both locally and globally. Techniques such as STM AFM have proven to be really useful in this task, producing some of the most exciting findings in these unique materials.

In this work we plan to develop a new scanning tunneling microscope/atomic force microscope (STM-AFM) in Ultra-High-Vacuum (UHV) conditions, specifically designed to track, with atomic resolution, the same sample region from 4K to 400K, and also to position, with few micrometer precision, in a given sample region. The combination of these capabilities, unique in this kind of microscopes, will enable, on one hand, to track the evolution of the sample properties in an exceptionally wide range of temperatures and, on the other, to measure 2D samples with a much reduced total size that could be placed over insulating substrates



in order to gate them.

Fig 1. a) 3D representation of the full microscope. The sample is upside-down and the tip is approached to it to measure. **b)** Zoom of the head of the microscope with the Kolibri mounted on top of the piezotube.

Quantum Well Edge States in Graphene Nanoribbons

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Graphene nanoribbons (GNRs) can be synthesized on metal surfaces with atomic precision using on surface synthesis techniques. Their precise size and shape can be tuned finely by selecting appropriate precursor molecules. The incorporation of additional functional molecules during the on-surface synthesis allows the creation of hybrid systems. In earlier work [1], we demonstrated the creation of such hybrid systems by contacting magnetic porphyrin molecules with chiral (3,1)-GNRs on Au(111). However, in that work it was not analyzed in depth, to what extend the electronic bandstructure of the connecting GNRs is affected.

Here, we present results from Fourier-transformed tunneling spectroscopy performed along the axis of a GNR segment enclosed by two porphyrins. We show that the presence of porphyrin creates a quantum well system, resulting in discrete resonant edge-states in the electronic bandstructure. We find a quadratic dispersion relation and extract from that an effective electron mass close to the one found in pristine ribbons.

References:

[1] Li et al. Science Advances 4, eaaq0582 (2018)

Domains and boundaries in graphene nanostructures

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Understanding grain boundaries in polycrystalline graphene is crucial for the control of both their electronic and mechanical properties. Depending on their topological structure, boundaries can affect transport across grains [1], or host their own one dimensional metallic states [2]. Concerning mechanical stability, they can either weaken or strengthen the graphene sheet [3]. In graphene nanostructures, the role of structural defects is even more critical. At this scale, boundary and edge energetics may additionally impose different stability and kinetic landscape from that at the macroscale [4], making their study fundamental for the control of physical and chemical properties.

We here report experimental evidence on some predicted and other new topological defect boundary structures, as found by Scanning Tunnelling Microscopy (STM) in graphene nanoislands grown on Ni(111) by CVD [5]. At mild annealing temperatures, we obtain multi-domain nanoislands with topological and continuous strained domain boundaries. The most common topological defects are 57 linear and ring boundaries and 558 linear boundaries, where transparency to Dirac electrons [1], quantum dot confinement [6], and 1D metallic states [7] have been predicted respectively. High-resolution STM images allow us to characterize both the stacking and orientation of graphene domains and the boundary atomic structure. By comparing a statistical analysis of the rotated domains to grain-boundary energies [8], we conclude that the selection of rotational domains is determined by boundary rather than stacking energetics.

References:

- [1] Yazyev, O. V et al., Nature Mater. 9, 806 (2010)
- [2] Luican-Mayer A. et al., 2D Mater., 3, 031005 (2016); W. Jaskolski et al., Nanoscale , 8 (2016) 6079
- [3] Wei Y. et al., Nature Mater., 11, 759 (2012)
- [4] A. Garcia-Lekue et al., J. Phys. Chem. C , 119 1 (2015)
- [5] S. O. Parreiras et al., 2D Mater., **4** 25104 (2017)
- [6] Cockayne, E. et al., Phys. Rev. B 83, 195425 (2011)
- [7] Lahiri, J. et al. Nature Nanotech., **5**, 326 (2010)
- [8] Yazyev O. et al., Phys. Rev. B, **81**, 195420 (2010)



Fig 1. STM scans of graphene grain-boundaries in nanoislands on Ni(111). Different types of topological defect boundaries consisting on pentagon/heptagon units separate (a) stripes and (b) quantum dots of domains with 30° of relative rotation, while (c) double pentagon/octagon units and (d) continuous strained boundaries separate non-rotated domains in different stacking configurations.

STM/AFM study of local work function variations on h-BN/Cu(111)

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The adsorption of single atoms or molecules on surfaces is mediated by their interaction with the substrate. The surfaces must, therefore, be characterized and understood from the structural, chemical and electronic point of view. In this respect, the nanometer scale local work function variations of the hexagonal boron nitride (h-BN) decoupling layer have been used for explaining favourable adsorption sites and molecular arrangements [1,2]. Using a tuningfork based combined STM/AFM at 1 K base temperature, we study h-BN on a Cu(111) substrate. We find bias dependent electronic corrugations by analyzing constant current and constant height STM images. We compare the local work function variation obtained by field emission resonance states [3] and complimentary Kelvin probe force microscopy at the different areas of this corrugation. Analyzing three-dimensional force maps we do not observe the soft stiffness previously found on h-BN/Rh(111) samples [4].

References

- H. Dil, J. Lobo-Checa, R. Laskowski, P. Blaha, S. Berner, J. Oster-walder, and T. Greber, Science 319, 1824 (2008).
- [2] P. Jacobson, T. Herden, M. Münks, G. Laskin, O. Brevko, V. Stepanyuk, M. Ternes, and K. Kern, Nat. Comm. 6, 8536 (2015).
- [3] S. Joshi, D. Ecija, R. Koitz, M. Iannuzzi, A. P. Seitsonen, J. Hutter, H. Sachdev, S. Vijayaraghavan, F. Bischoff, K. Seufert, J. V. Barth, and W. Auwärter, Nano Lett. 12, 5821 (2012).
- [4] T. Herden, M. Ternes, and K. Kern, Nano Lett. 14, 3623 (2014).



a.) Φ variation map using the shift in first FER peak from dZ/dU spectra ($\Delta\Phi$ =245 meV). b.) Φ variation map of the Contact Potential Difference obtained using constant height KPFM measurements on the grid ($\Delta\Phi$ =175 meV). c.) Selected frequency shift images from a set of constant height measurement for determining the effective stiffness of the 2D monolayer.



Ζ

Frequency shift image

BihurCrystal

<u>Elizabeth Goiri</u>

Controlled tautomerization of molecules on graphene

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The understanding of molecular excitation on surface is of paramount importance for the achievement of functional surfaces and information storage at the molecular scale [1]. Molecules on graphene can be used to tune its properties or to realize functionalized carbon surfaces. Tetraphenyl porphyrin molecules (H₂TPP) on graphene can assemble to form organized monolayer islands. Within this molecular lattice, two molecular configurations coexist. The H₂TPPs are made of a macrocycle group containing two inner hydrogen atoms. These atoms can switch between two positions leading to tautomer conformations. These two states can be clearly distinguished in STM topographic images when tunneling through their HOMO state. Further, it is possible to reversibly switch the molecules between the two tautomer configurations by means of controlled voltage pulse using STM tip [2]. A plot of current vs time reveals these two states as discrete levels and the random switching as a telegraph signal. It is possible to perform STM images without switching the molecules using an appropriate bias voltage for the imaging setpoint. Combining imaging at non-perturbative bias voltage and writing by applying a voltage pulse above selected molecules, it is possible to manipulate the state of every single molecule and write an artificial pattern within the molecular island. This allows to test the stability of the molecular conformation over time, revealing that no spontaneous switching occurs at 5K when no excitation is applied by the STM tip. The energy barrier for such process is predominantly dictated by the molecular energy levels on graphene. By analyzing the distribution of lifetime of the molecule for the two states, it is possible to draw insights about the excitation process of these molecules on graphene.

- Peter Liljeroth et. al, Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules Science (31 Aug 2007) Vol. 317, Issue 5842, pp. 1203-1206
- [2] Van Dong Pham et. al, Control of Molecule–Metal Interaction by Hydrogen Manipulation in an Organic Molecule *J. Phys. Chem. Lett.*, (**2016**) 7 (8), pp 1416–1421



Fig-1. (a) STM topography image of a porphyrin (H_2 TPP) island on graphene (taken at -1.5V and 20 pA) manipulated using voltage pulse to highlight "2018" feature using a combination of the two tautomeric configuration (b) STM topography image (-1.5V, 20pA) of the two tautomers distinguished by bright and dark contrast, and superimposed with their corresponding chemical configuration. (c) A typical current-time plot of the tunneling current illustrating the random switching events of porphyrin molecules.

Mapping the conductance of electronically decoupled graphene nanoribbons

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With the advent of atomically precise synthesis and consequent precise tailoring of their electronic properties, graphene nanoribbons (GNRs) have emerged as promising building blocks for nanoelectronics. Before being applied as such, it is imperative that their charge transport properties are investigated. Recently, formation of a molecular junction through the controlled attachment of nanoribbons to the probe of a scanning tunneling microscope (STM) and subsequent lifting allowed for the first conductance measurements.[1,2] Drawbacks are the perturbation of the intrinsic electronic properties through interaction with the metal surface, as well as the risk of current-induced defect formation which largely restricts the measurements to off-resonant transport. We show that resonant transport – essential for device applications – can be measured by lifting electronically decoupled GNRs from an ultrathin layer of NaCl. By varying the applied voltage and tip-sample distance, we can probe resonant transport through frontier orbitals and its dependence on junction length. This technique is used for two distinct types of GNR: the 7-atom wide armchair GNR and the 3,1-chiral GNR. Besides mapping the conductance, we demonstrate that we can simultaneously measure the current decay with increasing junction length and bias voltage by using a double-modulation spectroscopy technique.

References:

- [1] Koch, M., Ample, F., Joachim, C. & Grill, L. Voltage-dependent conductance of a single graphene nanoribbon. *Nat. Nanotechnol.* **7**, 713–7 (2012)
- [2] Jacobse, P. H. *et al.* Electronic components embedded in a single graphene nanoribbon. *Nat. Commun.* 8, 119 (2017)



Fig 1. Schematic representation of conductance mapping experiments on 3,1-chiral graphene nanoribbons. The model shows a junction of a nanoribbon lifted by the STM tip from a patch of sodium chloride. The inset shows a conductance map recorded as a function of bias voltage and tip height (dI/dV(V,z)).

Revealing a formation of 2D superstructure on the oxygen-rich surface of α -Fe₂O₃(0001)

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The surface of metal oxides reconstructs in many ways depending on the crystallographic planes and preparation procedures. In the case of iron oxides, the surface reconstruction of α -*Fe*2O3(0001) is still controversial. Under oxidizing conditions, it partially reconstructs in the so-called "biphase" structure, which traditionally has been explained by the coexistence of small islands of FeO and *Fe*2O3(0001). Furthermore, other phases are present, and there is no recipe to obtain large domains of single phases on the surface, which hinders an unambiguous interpretation of spectroscopic and microscopy data.

In this work, we present a procedure to obtain micrometer-sized domains of single stoichiometry under reducing and oxidative conditions. This has allowed us to thoroughly characterize the two main phases of the α -*Fe*2O3(0001) by means of STM, AFM, LEEM, µLEED, XPS, and NEXAFS and DFT calucaltions. Moreover, we have solid evidence that that the "biphase" structure may, in fact, be a novel 2D material rather than a truncated bulk. Complementary DFT calculations support the model of an O-Fe-O trilayer (*FeO*2) on the surface.



Fig 1. (a) STM image reveals honeycomb superstructure with periodicity of 41 Angstrom with two rotational domains. (b-c) The presence of the superstructure is further confirmed by STM-FFT and μ LEED measurements (b-c).

Theoretical prediction of novel 2D materials with uique electronic properties

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The discovery of graphene and its remarkable properties, has stimulated interest in other 2D materials, giving rise to a fertile field of research. Here we present a theoretical prediction of two different 2D materials. On the one hand, we propose a new class of metallic two-dimensional compounds: carbides and nitrides of Co and Ni.¹ These phases are p4g clock reconstructed, and contain planar tetracoordinated C or N, very uncommon especially in extended systems (Fig. 1, left). We show that these materials owe their stability to local triple aromaticity (π , σ -radial, and σ -peripheral) of the M₄X (M = Co, Ni, X = C, N) unit that main group elements. All of them are metallic and, as a matter of fact, cobalt carbides and binds the nitrides are ferromagnetic, a rare property in 2D systems. We propose that these monolayers could be prepared through surface deposition and peeling, possibly on a metal with a larger lattice constant metal, like Ag. On the other hand, a new 2D boron that could be grown on the surface of W(110) is reported.² This boron monolayer is composed of hexagons and squares (Fig. 1, right), has remarkable properties, like anisotropic electric conductivity, and it is therefore a promising material for technological applications. Overall, these new 2D materials not only have interesting electronic properties, but they are predicted to be highly stable. Indeed, using ab-initio molecular dynamics simulations we found that all these systems are stable up to at least T = 1800 K.

- [1] Jimenez-Izal, E.; Saeys, M.; Alexandrova, A. N. J. Phys. Chem. C 120, 21685-21690 (2016)
- [2] Cui, Z.; Jimenez-Izal, E.; Alexandrova, A. N. J. Phys. Chem. Lett. 8, 1224 (2017)



Fig 1. The proposed new 2D structures: metallic M₄X₂ monolayer (right) and B sheet (left).

Sources of suppressed quasiparticle interference signals

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Quasiparticle interference (QPI) patterns arising from scattered electronic states on the surface of a crystal are experimentally accessible with scanning tunneling spectroscopy. The energy dependence of the standing waves is directly linked to the band structure of the material. Further insights are obtained when expected QPI signals are extinguished or have a characteristic peak shape. Here we demonstrate how (i) spin, (ii) pseudospin, (iii) layer polarization and (iv) forward scattering lead to strongly reduced QPI signals. The materials studied here are monolayer and bilayer graphene, as well as the two-dimensional surface state of the topological insulator $BiSbTeSe_2$. Additionally, material-dependent parameters, such as the screening length and scattering rates, are obtained when comparing experimental maps with theoretical models based on the *T*-matrix theory. The latter also provides a general peak-fitting function for QPI patterns in *k*-space.



Fig 1. QPI maps of monolayer and bilayer graphene, which are recorded in real space and analyzed in *k*-space.

Emergent surface magnetism on symmetry broken metallic surface of PdCrO₂

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PdCrO₂ with delafossite structure has an intriguing three-dimensional spin order in the layered triangular Cr lattices. Interestingly, the surface magnetism of metallic delafossite is very distinguishable from the bulk because of the broken inversion symmetry [1,2]. We performed Spin-polarized STM (SP-STM) study on the two equally possible cleaved surfaces terminated with CrO₂ and Pd. On the CrO₂-terminated surface where direct tunneling to the Cr verified, we could observe no long-range magnetic order, which can be explained by the CrO₂-terminated surface with no Pd upper layer having different super exchange interaction compared with the bulk CrO₂ case. However, on the Pd-terminated surface with irregular hexagonal surface reconstruction, signatures of spin textures of two distinct origins are revealed. In filled state dominated by localized 4d-orbitals of Pd, we observed spin texture induced by proximity effect associated with the underlying $\sqrt{3} \times \sqrt{3}$ magnetic order in the CrO₂ layer. In empty state dominated by 5s-orbital of Pd, we could observe an emergent spin state with high spin polarization on the perimeters of the hexagonal Pd islands mediated by broken symmetry. Our findings provide a new type of surface spin texture induced by dislocations and suggest routes to controlling spin states by various broken symmetries in customized oxide heterostructures.

- [1] Veronika Sunko *et al.* Maximal Rashba-like spin splitting via kinetic-energy-coupled inversionsymmetry breaking, Nature **549**, 492–496 (2017)
- [2] F. Mazzola *et al.* Itinerant ferromagnetism of the Pd-terminated polar surface of PdCoO₂ arXiv:1710.05392v1

Tailoring end states of graphene nanoribbons by metal atoms

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Carbon-based nanomaterials have appeared being a substitute of semiconducting silicon for applications in advanced electronics. Graphene nanoribbons (GNRs), narrow strips of graphene, in particular have been shown to exhibit exotic electronic and magnetic properties relating to their edge geometries, width, and end terminations. While small variations in the edge topology, or the width may translate ribbons into unusual magnetic properties, changes in the band structure can be attained by placing dopant heteroatoms into the covalent cage of ribbon edges. Here we explore the role of the dopants in site specific modification of electronic states in armchair graphene nanoribbons with consequent tailoring of the density of states localized at the ends of their zigzag edges. Using a scanning tunneling microscope, we manipulate isolated metal atoms to be placed underneath ribbons, achieving an atomic precision in tuning the ribbons electronic and magnetic properties-- an important step towards the realization of engineered materials for electronics applications.

Structural and electronic characterization of sulfur depleted monolayer VS₂ synthesized on Au(111)

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Studies on bulk transition metal dichalcogenides (TMDCs) show a variety of electronic properties based on the specific combination of metal and chalcogen elements. Since it is possible to obtain stable 2D version of many TMDCs, they attracted great attention for the opportunity to study reduced dimensionality in a variety of electronic systems. VS₂ is of particular interest, as it has not been synthesized in monolayer form, and it is unclear what the magnetic ground state of it is. Here, we present an investigation with low temperature scanning tunneling microscopy/spectroscopy (STM/STS) on structural and electronic properties of sulfurdepleted single layer VS₂/Au(111) surface. Upon annealing as grown 1T monolayer VS₂, there is a structural phase transition which corresponds to a depleted phase of VS₂. This results in depletion of sulfur from the surface layer, as manifested by reconstructed surface which exhibits chain like structures. Our results shed light on the atomic structure of single layer VS₂ as well as reveal a complex striped phase at low energies which may be a signature of complex magnetic order. STS mapping at low temperature indicates the emergence of non-dispersive electronic ordering close to the Fermi level. We will also discuss current SP-STM experiments to shed further light on the magnetic order in this system.

An electrically controlled single atom magnetic switch on black phosphorus

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Single atoms at the surfaces of solids have demonstrated rich electronic¹, chemical², and magnetic³⁻⁵ properties. In this direction, we demonstrate that we can manipulate the orbital population of a single cobalt atom on a crystalline black phosphorus surface. Using the local electric field generated from an STM tip, individual cobalt atoms residing at the same hollow site can be reversibly switched between two stable states, which correspond to the different orbital configurations. The experimentally observed charge density of each configuration (fig. 1) is corroborated with density functional theory calculations, which reveal distinct high and low total magnetic moments for each state, as well as the electronic properties of the cobalt atom which locally dopes the black phosphorus. We investigate the stability of each configuration, as well as compare the experimentally measured impurity states with DFT calculations. Finally, we study the switching dynamics to determine the underlying mechanism and energy scale of the switching. This system opens up the horizon to explore complex memory based on both the orbital and spin degrees of freedom.

- [1] Koenraad, P. M. & Flatté, M. E. Single dopants in semiconductors. Nat. Mater. 10, 91–100 (2011)
- [2] Kyriakou, G. *et al.* Isolated metal atom geometries as a strategy for selective heterogeneous hydrogenations. *Science* **335**, 1209–1212 (2012)
- [3] Rau, I. G. et al. Reaching the magnetic anisotropy limit of a 3d metal atom. Science 344, 988–992 (2014)
- [4] Donati, F. et al. Magnetic remanence in single atoms. Science **352**, 318–321 (2016)
- [5] Natterer, F. D. et al. Reading and writing single-atom magnets. Nature 543, 226–228 (2017)





Fig 1. Cobalt on graphene in J_{low} and J_{high} configurations.

STM Study of Exfoliated Few Layer Black Phosphorus Annealing in Ultrahigh Vacuum

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After its exfoliation in 2014, black Phosphorus (bP) has emerged as a very interesting new member in the family of two-dimensional (2D) materials, due to its unique properties like layer-number-driven bandgap tunability and in-plane anisotropy. Surface-science studies on this material are of great interest for the bP community, but they are hindered by its high reactivity to oxygen and water, a major challenge to scanning tunneling microscopy experiments. As a consequence, the large majority of these studies have so far been realized by cleaving a bulk crystal in situ under vacuum¹⁻³. Here we present a study of surface modification on exfoliated bP flakes upon subsequent annealing steps, up to 550 °C, well above the sublimation temperature. In particular, our attention is focused on the temperature range around 375 $^{\circ}$ C - 400 $^{\circ}$ C, when sublimation starts, and a controlled desorption from the surface occurs with the formation of characteristic well-aligned craters. There is an open debate in the literature about the crystallographic orientation of these craters, i.e. whether they align along the zig-zag⁴ or the armchair⁵ direction. Thanks to the atomic resolution provided by scanning tunneling microscopy, we are able, with a direct measurement, to identify the crystallographic orientation of the crystal with respect to the craters, and thus, their alignment: the long axis of the craters is aligned along the [100] (zig-zag) direction of bP. This allows us to solve this controversy, and, moreover, to provide insight in the desorption mechanism, since different mechanisms (namely P or P_2 desorption) lead to different orientations of the craters.

References:

- [1] Liang, L. et al., Nano Lett. 14, 6400 (2014).
- [2] Yau, S.-L. et al., Chem. Phys. Lett. 198, 383 (1992).
- [3] Zhang, C. D. et al., J. Phys. Chem. C 113, 18823 (2009).
- [4] Fortin-Deschenes, M. et al., J. Phys. Chem. Lett. 7, 1667 (2016). [5] Liu, X. et al., J. Phys. Chem. Lett. 6, 773 (2015).



Fig 1. (a) Illustration of sublimation of phosphorus dimers from bP surface, forming craters with long axis parallel to [100] zig-zag crystallographic direction. (b) RT STM data showing atomically resolved images of bP surface near monolayer deep craters, providing crystallographic direction for crater orientation and underlying desorption mechanism.

Effects of Monolayer Bi on the Self-Assembly of DBBA on Au(111)

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The initial growth behaviors of nonplanar 10,10'-dibromo-9,9'-bianthryl (DBBA) molecules on the Au(111) substrates, which is either pristine or Bi- $3 \times \sqrt{3}$ -Au(111), at low deposition rates have been systematically investigated using low-temperature scanning tunneling microscopy (LT-STM), Photoemission spectroscopy (PES) and density functional theories (DFT) calculations. On Au(111), upon coverage increasing, DBBA single-molecule chains along $<11\overline{2}>_{Au}$ collectively transit into double-molecule chains along $<1\overline{10}>_{Au}$, revealing the delicate competing between intermolecular interactions and molecule-substrate interfacial interactions. On Bi- $3 \times \sqrt{3}$ -Au(111), DBBA molecules self assemble into an unique hexamer phase due to the enhanced intermolecular interactions via C-H... π and halogen bonds. DFT calculations confirm the proposed molecular configuration change of single DBBA molecule when adsorbed on different substrates. The effects of such substrates on the subsequent graphene nanoribbons (GNRs) formation are addressed.

- Huang, H. et al. Spatially Resolved Electronic Structures of Atomically Precise Armchair Graphene Nanoribbons. Sci. Rep. 2, 983(2012)
- [2] Tian G., Huang H*. et al. Effects of monolayer Bi on the self-assembly of DBBA on Au(111). Sur. Sci. 665 (2017) 89–95
- [3] Tian Q. W., Huang H*. et al. in Preparation



Figure: self-assembled structures of DBBA

Magnetic transport properties of magnetic porphyrins connected to graphene nanoribbon electrodes

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Graphene and graphene nanoribbons (GNRs) are ideal systems for contacting functional molecules [1, 2] due to their extraordinary electron mobility and structural stability under high currents. In our previous work, we have shown the construction and magnetic characterization of a fully functional hybrid molecular system composed of a single magnetic porphyrin molecule covalently bonded to GNRs on a gold substrate [3]. To better exploit the functionality of the devices, the magnetic transport measurement of the device is needed. Here in this work, by modifying the molecular precursors, the magnetic porphyrins were fused into two GRNs electrodes in one-dimensional manner. The STM tip was used to contact one GNRs electrode and lift the functional hybrid devices from the surface to form transport junctions. By means of inelastic tunneling spectroscopy, we identify the presence of the spin states of the magnetic porphyrin in the transport junctions although the GNRs electrodes are semiconductor. And we find that the magnetic anisotropy energy does not depends on length of the GNRs electrodes, but it is related to the d orbital of the magnetic porphyrin due to the e-e interactions.

Reference:

- [1] J. A. Mol, et al, Nanoscale 7, 13181–13185 (2015)
- [2] C. Jia, et al, Science 352, 1443–1445 (2016)
- [3] J. Li, et al, Sci. Adv. 4, eaaq0582 (2018)



Fig. 1. (a) model structures of molecular precusors used in the experiment. (b) STM current image of a magnetic porphyrin fused to GNRs electrodes (taken at 2 mV in constant height mode with a CO-terminated tip). (c) illustrations of the magnetic transport measurements.

Structure and Electronic Properties of Intrinsic Defects in Single Layer Molybdenum Disulfide on Au(111)

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Transition metal dichalcogenides (TMDCs) are two-dimensional materials with a natural band gap, making them interesting as sensors, solar cells or LEDs. Single layer molybdenum disulfide (MoS_2) is especially interesting, because it provides a direct band gap [1] and a strong spin-splitting of the valence and conduction band.

Here, we grow MoS_2 epitaxially on a Au(111) surface as described in [2]. Using combined scanning tunneling/atomic force microscopy (STM/AFM) at low temperatures, we observe different kinds of defects. Particularly prominent are defects, which appear in sizes of several nanometers. NC-AFM reveals an atomically intact surface layer, suggesting that the origin of the defect is located at the gold interface. At these sites, the band gap of MoS_2 is significantly modified, pointing towards quasi-freestanding MoS_2 on a metal substrate [3].

Moreover, we identify single point defects like interstitial atoms and S vacancies by STM/AFM and tunneling spectroscopy. The latter exhibit localized in-gap defect states and show agreement with predictions from density functional theory simulations [4,5,6].

- [1] Mak, et al., PRL 105, (2010) 136805
- [2] Sorensen, et al., ACSNano 8, (2014) 6788
- [3] Krane, et al., Nano Lett. 16, (2016) 5163
- [4] Fuhr, et al., PRL 92, (2004) 026802
- [5] González, et al., Nanotechnology 27, (2016) 105702
- [6] N. Krane, C. Lotze, A. Yousofnejad, G. Reecht, P. Pou, B. Biel and K. J. Franke (in preparation)

Atomic-Scale study of impact of Boron and Nitrogen dopants in graphene chemical reactivity by STM/AFM/KPFM and DFT calculations

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Controllable incorporation of nitrogen and boron heteroatoms in graphene provides donor and acceptors centers tuning its electronic, magnetic properties and chemical reactivity with potential application on storage energy and molecular sensors [1]. Despite the enormous interest developed, an atomistic investigation of the doped graphene chemical reactivity is missing.

We report our combined experimental Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM) measurements at 5K in Ultra High Vacuum (UHV) of Nitrogen and Boron co-doped graphene on SiC(0001) [2]. Our atomically resolved AFM images with CO-functionalized tip, reveal a very distinct contrast for graphitic N and B dopants attributed to electron density variations. This finding is corroborated by both experimental and calculated interaction energy at the dopant sites which is dominated by the electrostatic potential. Additionally, a shift in the local work function as a result of lend-accommodation of electrons from the graphene to the dopants is observed by means of KPFM measurements [3]. Remarkably, we map the in- and out- of the plane electrostatic potential of the dopants highlighting the relevance of the polarization for tuning chemical reactivity of graphene. The incorporation of a B dopant in a stable Stone-Wales configuration is identified by KPFM experiments and DFT calculations.

References:

- [1] Georgakilas, V. et al. Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. Chemical Reviews 112, 6156–6214 (2012)
- [2] Telychko, M. et al. Achieving High-Quality Single-Atom Nitrogen Doping of Graphene/SiC(0001) by Ion Implantation and Subsequent Thermal Stabilization. ACS Nano 8, 7318–7324 (2014)
- [3] Gross, L. et al. Measuring the Charge State of an Adatom with Noncontact Atomic Force Microscopy. Science 324, 1428–1431 (2009)



Fig 1. (a) High resolution STM image of Boron and Nitrogen co-doped graphene/SiC(0001). (b) High resolution AFM image with a CO-functionalized tip of the area marked in (a).

Direct observation of physisorbed H₂ on Graphene

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Hydrogen storage is a key issue in the development of fuel-cells that use hydrogen as energy carriers. Graphene is a promising hydrogen adsorbent owing to its light weight, high surface area and tailorable structure. Physisorbed hydrogen molecules on graphene, having low adsorption and desorption barriers, especially attract the attention of many researchers. To understand the chemical and physical properties of these molecules, direct probing of adsorbed species at the atomic scale is essential, for which STM has been proven to be an ideal tool. However, due to its instability and invisibility, it is very challenging to measure physisorbed molecular hydrogen on graphene with STM. Here, we present a direct observation of hydrogen molecular showed pronounced features in the differential conductance spectra which exhibit negative differential resistance. The absorption geometry of the hydrogen molecules were determined based on the location and relative intensity of the inelastic tunneling spectroscopy (IETS) peaks which correspond to the rotational modes. Furthermore, by varying the charge carrier density on the graphene surface at different current set points, we were able to investigate the influence of the tunneling current and the electric field on the adsorption geometry of H₂ molecules.

Edge states in chiral-shaped graphene nanoribbons

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Understanding the configuration of electrons in confined graphene nanoribbons (GNRs), and the physical phenomena beneath, is still a challenging quest. Among all the graphene-like ribbons studied to date, chiral-shaped GNRs (i.e. with periodically alternating armchair and zigzag-like segments) represent the most scarcely explored ones. Here we present several routes for constructing chiral nanoribbons with different widths using on-surface synthesis techniques [1].

Recently we reported the growth of narrow (3,1) GNRs (alternating 3 zigzag segments and 1 armchair) by deposing the 2,2'-dibromo-9,9'-bianthracene molecular precursor on different coinage metallic surfaces and annealing to relatively mild temperatures [2]. This chiral ribbon is semiconducting [3], presenting a small gap of 670 mV. Here we present the (on-surface) synthesis of wider chiral GNRs (cGNRs) by using molecular precursors with additional anthracene units. Using scanning tunneling spectroscopy we demonstrate that the width strongly determines the formation and shape of electronic edges states.

References:

- [1] Talirz et al., Adv. Mat. 28, 6222-6231 (2016).
- [2] D. G. de Oteyza et al., ACSnano 10, 9000-9008 (2016).
- [3] N. Merino-Díez et al., J. Phys. Chem. Lett. 9, 25-30 (2018).



Fig 1. Constant height maps with a CO-functionalized STM tip of the structures studied in this work. Models of the unit cells are superimposed in every case. (a-c) (3,1)-cGNRs with varying width of (a) Nz=4, (b) Nz=6 and (c) Nz=8, where Nz represents the common convention for describing width in zigzag-shaped GNRs.

On-surface synthesis and scanning tunneling microscopy studies of open-shell graphene nanostructures

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Topologies of the edge and π -electron array are paramount in determining the electronic properties of polycyclic aromatic hydrocarbons (PAHs). Distinctive topologies result in appearance of unpaired electronic densities on corresponding PAHs, and such systems constitute the family of open-shell graphene nanostructures^[1,2]. Synthesis of open-shell systems is appealing both from a fundamental physics point-of-view, and towards potential application in optoelectronic and spintronic devices. However, their high reactivities make a solution-based synthetic approach difficult. In this respect, on-surface synthesis under ultra-high-vacuum conditions on noble metal substrates provides a valuable synthetic toolbox to fabricate such systems and characterize them *in situ* with advanced scanning probe techniques.

In this contribution, we show examples of some novel open-shell systems, ranging from onedimensional linear acenes to quasi-two-dimensional architectures. We utilize non-contact atomic force microscopy and functionalized-tip STM imaging to reveal structural details, and unravel the electronic properties of the systems under investigation with scanning tunneling spectroscopy. Our results, supported by mean-field and many-body perturbation theory calculations, reveal interesting properties in these systems including low electronic gaps and size-dependent evolution of open-shell character.

References:

- [1] Benzenoid Quinodimethanes. Konishi, A. & Kubo, T. Top. Curr. Chem. (2017) DOI: 10.1007/s41061-017-0171-2
- [2] Closed-shell and Open-shell 2D Nanographenes. Sun Z. & Wu J. In: Siegel J., Wu YT. (eds) Polyarenes I. Topics in Current Chemistry, vol 349. Springer (2012)

[3]



Fig. 1. Electronic properties of higher acenes, one of the open-shell systems studied in this contribution. Length-dependent electronic gap of acenes and comparison with computed quasiparticle gaps for open- and closed-shell configurations. Inset: nc-AFM image of nonacene.

Probing the band structure of quasi-freestanding monolayer MoS₂

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We epitaxially grow high-quality molybdenum disulfide (MoS₂) monolayers on graphene on Ir(111) [1], and probe its electronic structure with low temperature scanning tunnelling spectroscopy (STS).

A bandgap of 2.50 ± 0.05 eV is measured by STS, showing the freestanding nature of MoS₂ on this substrate. Furthermore, by combining constant height and constant current STS modes and measuring the state-resolved tunnelling decay constant [2], we are able to disentangle the contributions of states located at various high-symmetry points, such as the spin-split valence band at the K-point. The band structure is found to be in close agreement with theoretical calculations for freestanding MoS₂, further evidencing the weak coupling with its Gr/Ir(111) substrate.

Additionally, the valence band is seen to undergo a stepwise bending towards line defects of the MoS_2 layer, such as mirror twin boundaries (MTB) and edges. We seek to explain and describe this behaviour with density functional theory and model Hamiltonians. This phenomenon could be of considerable significance to the TMDC heterojunction and devices communities.

- [1] Hall, J. et al., 2D Mater. 5, 025005 (2018)
- [2] Zhang, C. et al., *Nano Lett.* **15**, 6494 (2015)



Fig 1: (a) constant current STM topograph showing MoS₂ islands on graphene on Ir(111). Step edges in the Ir(111) can be seen vertically crossing the image. The bright, straight lines within the MoS₂ flakes are MTBs. Image size 165 x 183 nm², $U_{bias} = -1.5$ V, $I_{tunnel} = 50$ pA. (b) constant height STS performed on an MoS₂ monolayer, far away from any defects. The signal intensity is plotted in logarithmic and (inset) linear scales. $U_{set} = 1.5$ V, $I_{set} = 0.1$ nA. (a,b) adapted from [1].

Coexistence of charge order and quantum well states in MoSe₂ mirror twin boundaries

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One dimensional mirror twin boundaries (MTBs) on $MoSe_2$ are an ideal system to study low dimensional electronic order. We provide evidence for the coexistence of charge order [1] and quantum well states in MTBs using high-resolution scanning tunneling microscopy and atomic force microscopy (**Fig 1**). We compare the experimental data to a Hubbard model and demonstrate that the MTB quantum well states can be viewed as the small system-size limit of charge density waves. The model parameters sit close to the critical point at which the charge density wave gap closes. MTBs in MoSe₂ simultaneously demonstrate charge order at biases close to the gap, and quantum well states at moving away from the gap (**Fig 2**). The continuous evolution of charge order into quantum well states constitutes an example of a fundamental but uncommon finite size quantum phenomenon.

References:

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[1] "Charge density wave order in 1D mirror twin boundaries of single-layer MoSe₂". Sara Barja, Sebastian Wickenburg, Zhen-Fei Liu *et al.*, **Nature Physics** 12, 768 (2016).



Fig 1. (c) Mirror twin boundary (MTB) in monolayer $MoSe_2$ on graphene-terminated SiC. The metallic MTB has one extra Mo atom per unit cell. The modulation at ~ 3x the lattice periodicity arises from charge density wave (CDW) order. (d) CO-tip AFM image of finite MTB segments terminated by kinks and/or dislocations.



Fig 2. (a) A dI/dV spectrum at the MTB shows the LDOS of the metallic states near EF showing the 100 meV CDW gap. The pronounced satellite peaks (dashed lines), correspond to distinct energy states. (b) dI/dV map (V_s -110 meV) along the MTB (the corner bounds are just outside the image). This state shows 16 peaks. (c) the same MTB at the highest occupied state (Vs -70 meV) with 17 peaks. (d) the lowest unoccupied state (V_s +30 meV) with 18 peaks.

Inelastic spin flip spectroscopy of local spin moments in nanographenes

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Using ultrahigh-vacuum on-surface techniques, it is possible to synthesize nanographenes that are expected to host unpaired electronic spins. This includes triangular nanographenes [1], expected to have S = 1 [2], as well as graphene ribbons with zigzag edges [3], for which unpaired spins forming singlets are expected [4]. Here we address the question of how to probe these local moments using scanning probe microscopy. In particular, we address the inelastic electron tunneling spectroscopy (IETS) that has been successfully used to probe spin excitations of spin chains [5]. In this work we present our calculations modeling IETS for both graphene triangulenes and graphene ribbons, combining the cotunneling theory for IETS [6], and exact diagonalization of a Hubbard model to describe the nanographenes. We predict that IETS can efficiently map the spin-flip excitations along the structures, in analogy with experimental results on spin chains [7], permitting thereby an atomically-resolved characterization of these local spin moments.

- [1] N. Pavlicek, A. Mistry, Z. Majzik, N. Moll, G. Meyer, D. J. Fox and L. Gross. Synthesis and characterization oftriangulene. *Nature Nanotechnology* **12**, pages 308–311 (2017)
- [2] J. Fernández-Rossier and J. J. Palacios. Magnetism in Graphene Nanoislands. Phys. Rev. Lett. 99, 177204 (2007)
- [3] S. Wang, L. Talirz, C. A. Pignedoli, X. Feng, K. Müllen, R. Fasel and P. Ruffieux. Giant edge state splitting atatomically precise graphene zigzag edges. *Nature Communications* **7**, 11507 (2016)
- [4] R. Ortiz, N. A. García-Martínez, J. L. Lado and J. Fernández-Rossier. Electrical spin manipulation in graphene nanostructures. Preprint https://arxiv.org/abs/1712.07282
- [5] C. F. Hirjibehedin, C. P. Lutz and A. J. Heinrich. Spin coupling in engineered atomic structures. Science.312(5776): 1021-4 (2006)
- [6] F. Delgado and J. Fernández-Rossier. Cotunneling theory of atomic spin inelastic electron tunneling spectroscopy. Phys. Rev. B 84, 045439 (2011)
- [7] A. Spinelli, B. Bryant, F. Delgado, J. Fernández-Rossier and A. F. Otte. Imagin of spin waves in atomically designed nanomagnets. *Nature Materials* **13**, pages 782–785 (2014)

The FAST Module: An Add-On Unit For Driving Commercial Scanning Probe Microscopes To Video Rate And Beyond

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We present the design and the performance of an improved version of the FAST module, an add-on instrument that can drive commercial scanning probe microscopes (SPM) at and beyond video rate image frequencies, allowing the investigation of dynamical processes at surfaces with unprecedented time resolution [1]. In the design of this module, we adopted and integrated several technical solutions previously proposed by different groups in order to overcome the problems encountered when driving SPMs at high scanning frequencies [2]. The novelty of FAST is that it requires no modification of the existing scanner hardware and electronics, and its operation is totally transparent, allowing the user to switch immediately and seamlessly to the fast scanning mode when imaging in the conventional slow mode. The unit provides a completely non-invasive, fast scanning upgrade to common SPM instruments that are not specifically designed for high speed scanning. To test its performance, we thoroughly used this module to drive commercial scanning tunneling microscope (STM) systems (Omicron VT-STM and LT-STM, SPECS Aarhus) in a quasi-constant height mode up to frame rates of 100 Hz and above, in a temperature range between 77 K and 600 K, demonstrating extremely stable and high resolution imaging capabilities [3, 4]. The module is extremely versatile and its application is not limited to STM but can, in principle, be generalized to any scanning probe instrument.

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References:

- [1] https://fastmodule.iom.cnr.it/ Patent US8726409B2 and EP2428804B1
- [2] Dri, C. et al. Measurement Science and Technology 2012, 23, 55402; Esch, F. et al. Review of Scientific Instruments 2011, 82, 53702
- [3] Patera, L. L. et al. Science, Vol. 359, Issue 6381, pp. 1243-1246 (2018)
- [4] Patera, L. L. et al. Phys. Chem. Chem. Phys. 2017, 19, 24605; Patera, L. L. et al. Nano Lett. 2014, 15, 56-62



The FAST module is an add-on instrument to drive commercial scanning probe microscopes to video rate and beyond.



Fig 1. Schematics of the FAST module working principle.

Excitonic effects in monolayer 1T-TiSe₂ from hybrid density functional theory

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Transition metal dichalchogenides (TMDs), whether in bulk or monolayer form, exhibit a rich variety of charge-density-waves (CDWs) and larger periodic lattice distortions. While the actual role of nesting has been under debate, it is well understood that the microscopic interaction responsible for the CDWs is the electron-phonon coupling. The case of 1T-TiSe₂ is however unique in that the normal state above the critical temperature TCDW is characterized by a small quasiparticle bandgap as measured by ARPES, so that no nesting-derived enhancement of the susceptibility is present. It has therefore been argued that the mechanism responsible for this CDW should be different and that this material realizes the excitonic insulator phase proposed by W.Kohn. On the other hand, it has also been suggested that the phase diagram can be explained by a sufficiently strong electron-phonon coupling. In this work, in order to estimate how close this material is to the pure excitonic insulator instability, we quantify the strength of electron-hole interactions by computing the exciton band structure at the level of hybrid density functional theory, that has been shown to describe excitonic effects at least approximatively. We find that the indirect gap at Q_{CDW} is significantly reduced by excitonic effects, suggesting that electron-electron interactions indeed play an important role in the instability. We discuss the consequences of the results regarding the debate on the driving mechanism.

Chemical tuning of graphene properties: substrate mediated enhancement of the reactivity and inducing magnetism by combining nitrogen and oxygen dopants

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Graphene is commonly regarded as an inert material. However, using first principles calculations we unveil different ways of enhance its chemical reactivity and tuning its electronic properties which can be useful in the design of molecular electronics devices. For instance, we can use nitrogen defects to increase the reactivity of the layer creating preferential adsorption sites for oxygen trapping. We find interesting electronic properties in these oxygen-decorated nanopatterns, especially when more than one oxygen atom is absorbed and collective effects are displayed [1]. As a result, a magnetic solution, very similar to the state induced by the hydrogen adsorption, is stabilized (see figure). In addition, we show that it is also possible to induce a remarkable increment in the chemical activity of a graphene layer by simply growing it on an appropriate substrate [2]. In strongly-interacting substrates like Rh(111), graphene adopts highly rippled structures that exhibit clearly different areas with distinctive chemical behaviors. According to the local coupling with the substrate, we find areas whose properties resemble free-standing graphene, but also, more reactive regions leading to different pathways of adsorption and diffusion for both atomic and molecular oxygen.

- [1] C. Romero-Muñiz, et al.: (submitted)
- [2] C. Romero-Muñiz, et al.: (submitted)



Fig 1. Electronic properties of an oxygen-decorated nanopattern N-doped graphene (center) showing the magnetic solution revealed in the projected Dos (left). Theoretical STM image of the pattern (right).

Electroluminescence dynamics probed on a molecular scale

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Optoelectronic device performance is driven by nanoscale processes. Their dynamics can be studied with time-resolved techniques, many of which are, however, limited by spatial averaging. These limitations can be overcome by employing STM-induced luminescence (STML).

In this poster I will present a study of both plasmonic and excitonic (electron-hole pair recombination) electroluminescence on a C_{60} thin film grown on noble metal surfaces. The excitonic light originates from structural defects that act as charge and exciton traps. Such a single defect is a single photon emitter, whose spectrum has a sharp electron-hole recombination feature [1,2]. By measuring the effect of injecting individual charges on the electroluminescence with nanosecond voltage pulses, it is possible to follow the formation and recombination of single excitons [3]. In contrast to this mechanism, the plasmonic luminescence appears due to inelastic tunneling of electrons from the C_{60} layers the STM tip which excites a broadband cavity plasmon that decays radiatively.

These two light emission mechanisms can be combined to a bimodal light source (Fig. 1b) whose two components exhibit a different dependence on the dynamics of the injected charges. For low tunnel currents (several nanoseconds between charges) the exciton emission dominates the light intensity, while for higher currents the exciton is quenched due to exciton-charge annihilation, and the plasmonic component becomes dominant[4]. The methods presented here can be used to study the dynamics at the quantum limit of single charge injection also in other luminescent materials.

References:

- [1] P. Merino, C. Große, A. Rosławska, K. Kuhnke, K. Kern, , Nat. Commun., 6, 8461, 2015.
- [2] C. Große, P. Merino, A. Rosławska, O. Gunnarsson, K. Kuhnke, K. Kern, ACS Nano, 11, 1230-1237, 2017.
- [3] A. Rosławska, P. Merino, C. Große, C. C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, K. Kern, submitted.
- [4] P. Merino, A. Rosławska, C. Große, C. C. Leon, K. Kuhnke, K. Kern, submitted.



Fig 1. (a) Scheme of time-resolved STML set-up. Light induced by a nanosecond voltage pulses is detected with a single photon avalanche photodiode (SPAD) with ps time resolution. (b) Typical optical spectra of the exciton (upper), bimodal (middle) and plasmon (lower) luminescence.
Electron beam splitting with crossed graphene nanoribbons

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Graphene exhibits many exceptional mechanical and electronic properties that make it attractive for the fabrication of electronic devices at the nanoscale [1], but the gapless spectrum is a major obstacle for carbonbased electronic applications, since the absence of an electronic gap makes it a poor candidate to build logic electronic devices, e.g. field-effect transistor [2]. A gap can be however induced in different ways, among others, via lateral quantum confinement of the electrons, e.g., as it occurs in one-dimensional (1D) graphene nanoribbons (GNRs). On the other hand these GNRs can be produced [3] and manipulated [4, 5] with atomistic precision.

Here we analyze the effect of placing two GNRs one on top of the other interacting via the vander-Waals interaction (4-terminal device). Previous work based on DFT+NEGF [6] showed that electrons injected from one terminal can be split into two outgoing waves with a tunable ratio that strongly depends on the intersection angle between the ribbons. In this work we complement this by adopting a simple and numerically efficient tight-binding description that captures the essential physics [7]. In addition to the intersection angle, the precise stacking of the device results in a powerful tool to control the direction and intensity of the electron beam. Here we analyze different high-symmetry configurations as well as GNRs of varying width and edge chirality to reach a complete picture of the electron beam splitting effect.

References:

- A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.*, 81, 109–162 (2009).
- [2] F. Schwierz, *Nat Nano*, **5**, 487–496, (2010).
- [3] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Mullen and R. Fasel, *Nature*, 466, 470-479 (2010).
- [4] [M. Koch, F. Ample, C. Joachim, and L. Grill, Nat Nano, 7, 713–717 (2012).
- [5] S. Kawai, A. Benassi, E. Gnecco, H. Söde, R. Pawlak, X. Feng, K. Müllen, D. Passerone, C. A. Pignedoli, P. Ruffieux, R. Fasel, and E. Meyer, *Science*, 351, 6276, 957–961 (2016).
- [6] P. Brandimarte, M. Engelund, N. Papior, A. Garcia-Lekue, T. Frederiksen and D. SánchezPortal, *The Journal of chemical Physics*, **146**, 092318 (2017).
- [7] N. R. Papior, sisl: v0.9.2, https://github.com/zerothi/sisl/

Substrate-induced curvature effects and charge localization in monolayer MoS2

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Monolayer transition metal dichalcogenides (TMdCs) have attracted considerable attention due to their rigorous electronic and optical properties with spin and valley. For applications with TMdCs, environmental factors such as substrates or adsorbates are critical due to their low-dimensionality as a layered structure which are mostly exposed to the environment. Inevitably, the quasiparticle (or electronic) bandgap in monolayer MoS₂ exhibits variety due to dielectric screening or external strain effects from external factors. If we want to achieve the benefits of ideal monolayer TMdCs in applications, understanding the basic phenomena triggered by the extrinsic factors it is important to control and manipulate those. Here, we report an unusually large quasiparticle bandgap modulation of 1.23-2.65 eV from monolayer MoS₂ on Si substrate, which is induced by a substrate. By reduction of the quasiparticle bandgap due to substrate-induced bending strain or curvature in monolayer MoS₂, the direct bandgap in monolayer MoS₂ was eventually converted to an indirect bandgap above a bending strain of approximately 1.5%. Even for the small range of surface roughness of ~1 nm, curvature can be critical depending on the aspect ratio between height and width of hill or valley in MoS_2 . The observed bending strain in the top sulfur-layer was ranged from -6 to 6 %, which is within the observed linear elastic limit of 6-11%. By the bending strain, approximately 80% of the surface area revealed an indirect bandgap in contrast with the general belief of a direct bandgap in monolayer MoS_2 . Such a remarkable change in quasiparticle bandgap of MoS_2 was not observed in a flat substrate like HOPG. In addition, charge localization was observed along the curvature in monolayer MoS₂. DFT results support charge localization by curvature of MoS_2 and Fermi-level pinning-like behavior when MoS_2 are doped as shown in STS results. Photoluminescence and Raman spectroscopy were performed on MoS₂/SiO₂ with a cavity to investigate further in comparison with suspended MoS₂, which confirmed large variation in supported MoS₂ from those in suspended MoS₂ due to the surface roughness of substrate. It confirmed that substrate-induced curvature effects in atomic scale can be probed quickly and macroscopically by the optical methods. We, therefore, can easily qualify the flatness and modified electronic structures of monolayer MoS_2 over micrometer-scale, elucidating a strain-engineering of MoS₂ or other semiconducting 2D materials for future applications.



Syntheses and bandgap alterations of MoS₂ induced by stresses in grapheneplatinum substrates

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Epitaxially-oriented large-scale monolayer molybdenum disulfide (MoS_2) grown directly on graphene (Gr) with an atomic-clean interface draws intensive interest in both areas of fundamental sciences and electronic-device applications [1-3]. In general, however, synthetic characteristics and bandgap-related properties of MoS_2 crystals can be varied by the selection of substrates that support Gr, and mechanisms that govern these phenomena remain unclear. By means of scanning tunneling microscope and spectroscopy (STM/STS) and photoluminescence (PL) measurements, we have discovered that considerably-strained Gr can strongly affect the epitaxy of MoS_2 crystals and enhance the interlayer electronic coupling between monolayer MoS_2 and its Gr-platinum (Pt) substrate, leading to the stack of MoS_2 layers and a narrowing direct bandgap of monolayer MoS_2 . Our studies shed light on growing large-scale MoS_2 films on Gr and the bandgap modulation in these heterostructures.

References:

- [1] Miguel M. Ugeda, Steven G. Louie, Michael F. Crommie, *et al.* Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor. *Nature Mater.*, 2014, 13, 1091–1095.
- [2] Wen Wan, Han Huang, Weiwei Cai, *et al.* Syntheses and bandgap alterations of MoS₂ induced by stresses in graphene-platinum substrates. *Carbon*, 2018, 131, 26–30.
- [3] Wen Wan, Linjie Zhan, Weiwei Cai, *et al.* Temperature-Related Morphological Evolution of MoS₂ Domains on Graphene and Electron Transfer within Heterostructures. *Small*, 2017, 13, 1603549.



Fig 1. (a) Art illustration of the designed two-step procedure for growing of MoS_2 -Gr heterostructures on polycrystal Pt. (b) Stress-resulted different growing behaviors of MoS_2 crystals on Gr with/without cracks. (c) PL of MoS_2 on substrates of Gr-Pt, SiO₂, Gr-SiO₂, respectively. (d) STM images of monolayer MoS_2 grown on Gr. (e) Band structures of three positions from Gr to ML MoS_2 as selected in (d).

Hybridization of Yu-Shiba-Rusinov states in β-Bi₂Pd

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The coupling between spins in transition metal atoms and Cooper pairs in a superconductor gives rise to localized sub-gap excitations known as Yu-Shiba-Rusinov (YSR) states [1] [2] [3]. It has been proposed that the YSR states of proximal atoms hybridize [4], what can result in the formation of YSR bands. These bands are proposed as a platform to realize topological superconductivity in the presence of spin-orbit coupling or helical magnetic order and to host Majorana Zero-Energy Modes [5]. It is thus crucial to understand the basic mechanisms of YSR state hybridization in atomic nanostructures.

In this work we investigate the hybridization of YSR states in atomic-scale structures constructed by lateral manipulation on the surface of β -Bi₂Pd, a centrosymmetric s-wave superconductor. We use Mn adatoms as magnetic impurities, which show a single YSR state inside the superconducting gap. We find that Mn dimers show bonding and anti-bonding states as a result of the coupling between the constituent impurities and we track the evolution of these states in longer structures. From our results we conclude that Mn is a good candidate for the construction of atomic chains with extended bands and determine that only along certain directions the magnetic order might result in relevant non-trivial effects.

References:

- [1] L. Yu, Acta Physica Sinica 21, 75 (1965)
- [2] H. Shiba, Prog. Theor. Phys. 40, 435 (1968)
- [3] A. I. Rusinov, soviet Phys JETP 29, 1101 (1969)
- [4] M. E. Flatté and D. E. Reynolds Phys. Rev. B 61, 14810 (2000)
- [5] S. Nadj-Perge *et al.*, Science 34, 6209 (2014)
- [6] J. Kacmarcik et al., Phys. Rev. B 93, 144502 (2016)
- [7] D.-J. Choi et al., PRL 120, 167 (2018)



Fig 1. (a) STM data showing a manganese trimer constructed by lateral manipulation. (b) Spectroscopy along the trimer shows the evolution of YSR bound states and the formation of bonding and anti-bonding states.

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Scientific program at a glance

	Monday	Tuesday	Wednesday	Thursday	Friday
9:00 - 9:15	REGISTRATION				
9:15 - 10:00	Louie	Yazdani	Morgenstern		Brune
10:00 - 10:45	Crommie	Wahl	Pasupathy	Shih	Osterwalder
10:45 - 11:15					
11:15 - 12:00	Pascual	Wiesendanger	Stroscio	Michely	Fuhrer
12:00 - 12:20	Otero	Rubio-Verdú	Cortés	Barja	Lu
12:20 - 12:40	Mugarza	Ma	Tesch	Batzill	Mueller
12:40 - 13:00	García-Lekue	Choi	Jung Jung	Renard	Jo
13:00 - 15:00					
15:00 - 15:45	Veuillen	Pérez	Hofmann	Franke	
15:45 - 16:05	Courtois	Droghetti	Flicker	Biel	
16:05 - 16:25	Glatzel	de la Torre	Pásztor	Schuler	
16:25 - 16:45	Africh	Lagoute	Errea	Pizzochero	
16:45 - 17:15					
17:15 - 18:00	Fdez-Rossier		Wehling	Yazyev	
18:00 - 18:20	Andrei	POSTER SESSION	Tresca	Chirolli	
18:20 - 18:45					
20:45			CONFERENCE DINNER		

Venues

Conference

The workshop will take place in the **Miramar Palace** located in La Concha Bay in the city of San Sebastian.

Address: Paseo de Miraconcha, 48 Donostia-San Sebastián, Guipúzcoa Phone. +34 943 21 90 22 Web: http://palaciomiramar.eus/

<u>Lunch</u>

The lunch will take place in the **Barceló Costa Vasca Hotel** at 7-10 minutes walk from the Conference place.

Address:

Avenida Pio Baroja, 15 Donostia-San Sebastián, Guipúzcoa Phone: +34 943 31 79 50 Web: <u>https://www.barcelo.com/en-us/barcelo-hotels/hotels/spain/san-sebastian/barcelo-costa-vasca/</u>

Conference dinner

The Conference dinner will take place at **Ni neu restaurant**. Address: Zurriola Hiribidea, 1 Donostia-San Sebastian, Guipúzcoa Phone: +34 943 00 31 62 Web: http://www.restaurantenineu.com/en/restaurant/



Accommodation

Olarain residence

Address: Ondarreta Pasealekua, 24 Donostia-San Sebastian Phone: +34 943 00 33 00 Web: <u>http://www.olarain.com/</u>

San Sebastian hotel

Villa Alaidi residence

Address: Paseo de Hériz, 95, Villa Alaidi Donostia-San Sebastian Phone: +34 943 21 08 66 Web: http://www.villa-alaidi.com/





How to get to the N2D conference (follow "Summer Courses" indicators)



Access from Matia street (from A to C)

Entrance to the conference

The total route (7-10 mins)



Take the east exit from the palace



Take this side street







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NOVEL 2D MATERIALS EXPLORED VIA SCANNING PROBE MICROSCOPY & SPECTROSCOPY

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