O 90: 2D Materials VI: Growth, Structure and Substrate Interaction

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

O 90.1 Thu 15:00 MA 005

Growth of aligned and twisted hexagonal boron nitride on Ir(110) — •Thomas Michely, Jason Bergelt, Affan Safeer, Alexander Bäder, Tobias Hartl, and Jeison Fischer — II. Physikalisches Institut, Universität zu Köln, Köln, Germany

The growth of monolayer hexagonal boron nitride (h-BN) on Ir(110) through low-pressure chemical vapor deposition is investigated using low energy electron diffraction and scanning tunneling microscopy. Growth of aligned h-BN on Ir(110) requires a growth temperature of 1500 K, whereas lower growth temperatures result in coexistence of aligned h-BN with twisted h-BN. The presence of the h-BN overlayer suppresses the formation of the nanofaceted ridge pattern known from clean Ir(110). Instead, we observe the formation of a $(1 \times n)$ reconstruction, with n such that the missing rows are in registry with the h-BN/Ir(110) moiré pattern. Quantitative moiré analysis yields a precise determination of the moiré periodicity and the h-BN lattice parameter on Ir(110).

O 90.2 Thu 15:15 MA 005

Incommensurability and negative thermal expansion of single layer hexagonal boron nitride — •Marko Kriegel[1], Karim Omambac[1], Steffen Franzka[2], Frank Meyer zu Heringdorf[1,2], and Michael Horn-von Hoegen[1] — [1]Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany — [2]Interdisciplinary Center for Analytics on the Nanoscale (ICAN), Carl-Benz-Str. 199, 47057 Duisburg, Germany

The emerging field of straintronics, i.e., the control and utilization of the strain state of a 2D material, is of great importance for their technological development, specifically in view of their future incorporation into van der Waals heterostructures. To gain fundamental insights into structural peculiarities of two-dimensional systems, single layer hexagonal boron nitride (hBN) grown on Ir(111) by chemical vapor deposition was used as a prototypical model system: High-resolution reciprocal space mapping by SPA-LEED reveals the incommensurate nature of the material system by measuring the hBN in-plane lattice parameter, facilitated by the moiré magnification effect. In a growth temperature (T_g) regime of 700-1150 °C an average lattice parameter of 2.496±0.006 was found. Eventually, careful disentanglement of the hBN's and substrate's behavior for rising T_g allowed the determination of a negative thermal expansion coefficient of $\alpha_\mathrm{hBN} =$ -$2.4 \pm 1.2 \times 10^{-6}\,\mathrm{K}^{-1}$.[1]

[1] *M. Kriegel *et al. Appl. Surf. Sci.* **624** (2023) 157156

O 90.3 Thu 15:30 MA 005

Growth of high quality hexagonal boron nitride (*h*-BN) on surfaces of transition metals — Adrian Hemmi[1], •Ari Paavo Seitsonen[2], Michael S Altman[3], Marcella Iannuzzi[4], Thomas Greber[1], and Huanyao Cun[1] — [1]Physik-Institut der Universität Zürich — [2]Département de Chimie, École Normale Supérieure, Paris — [3]Department of Physics, Hong Kong Unversity of Science and Technology — [4]Chemie-Institut der Universität Zürich

The production of high-quality hexagonal boron nitride (*h*-BN) is essential for the ultimate performance of two dimensional (2D) materials-based devices, since it is the key 2D encapsulation material. We are working on the optimisation of the procedures to grow *h*-BN on surface of transition metals. Our recent achievements include the enhanced quality of the *h*-BN on Rh(111) via 2D distillation [*ACS Nano* **15**, 1351-1357 (2021)], and a decisive guideline for fabricating high-quality *h*-BN on Pt(111) [*Small* **18**, 2205184 (2022)]. We have found that it is crucial to exclude carbon from the *h*-BN related process, otherwise carbon prevails over boron and nitrogen due to its larger binding energy, thereupon forming graphene on metals after high-temperature annealing. We introduce the pyrolysis temperature T_p as an important quality indicator for *h*-BN on transition metals.

In order to understand better the underlying physical trends, we have performed systematic density functional theory calculations on 12 different hexagonally oriented transition metals [*Nanoscale Advances*, in Press; DOI: 10.1039/D3NA00472D]. We will discuss the experimental findings in light of the computed results.

O 90.4 Thu 15:45 MA 005

Formation of Europium-Ruthenium surface compound and protection of Eu below hexagonal boron nitride (h-BN) — •Alaa Mohammed Idris Bakhit[1,3] and Frederik Schiller[1,2] — [1]Centro de Física de Materiales CSIC-UPV/EHU-Materials Physics Center, E-20018 San Sebastián, Spain — [2]Donostia International Physics Center, E-20018 Donostia-San Sebastián, Spain — [3]Departamento de Física Aplicada I, Universidad del País Vasco UPV/EHU, E-20018 San Sebastián, Spain

We investigate the structural and electronic properties of Europium (Eu) intercalated beneath a layer of hexagonal Boron nitride (h-BN) atop of transition metal Ruthenium Ru(0001) substrate. The hBN monolayer was grown by the Chemical Vapor Deposition process on clean Ru(0001). To explore the structural aspects, we employed Low-energy electron diffraction (LEED). Our observations from LEED revealed c(4×2) and (2×2) superstructures emerging upon Eu intercalation, varying based on the Eu coverage. Simultaneously, the electronic structure was investigated by X-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission measurements (ARPES). Notably, XPS analysis post-Eu intercalation indicated the presence of Eu in a divalent valence state. Furthermore, we studied the possible protection of Eu by the h-BN layer on the Ru(0001) substrate. We observe that partially Eu can be protected but full protection was incomplete probably due to defects and h-BN growth boundaries which facilitated Eu oxidation.

O 90.5 Thu 16:00 MA 005

Real-Time Multiscale Monitoring and Tailoring of Graphene Growth on Liquid Copper — Valentina Rein[1], Mehdi Saedi[2], Maciej Jankowski[1], Anastasios Manikas[3], Francesco La Porta[1], Christos Tsakonas[3], Costas Galiotis[3], Gilles Renaud[4], Oleg Konovalov[1], and •Irene Groot[2] — [1]ESRF — [2]Leiden University — [3]University of Patras — [4]CEA

The synthesis of large, defect-free two-dimensional materials such as graphene is a major challenge toward industrial applications. Chemical vapor deposition on liquid metal catalysts is a recently developed process for the fast synthesis of high-quality single crystals of graphene. However, up to now, the lack of in situ techniques enabling direct feedback on the growth has limited our understanding of the process dynamics and primarily led to empirical growth recipes. Thus, an in situ multi-scale monitoring of the graphene structure, coupled with a real-time control of the growth parameters, is necessary for efficient synthesis. Here we report real-time monitoring of graphene growth on liquid copper (at 1370 K under atmospheric pressure conditions) via four complementary in situ methods: synchrotron X-ray diffraction and reflectivity, Raman spectroscopy, and radiation-mode optical microscopy. This has allowed us to control graphene growth parameters such as shape, dispersion, and the hexagonal supra-organization with very high accuracy. The presented results have far-reaching consequences for studying and tailoring 2D material formation processes on liquid metals during chemical vapor deposition.

O 90.6 Thu 16:15 MA 005

Imaging of topological defects in graphene grown by bottom-up synthesis — •Benedikt P. Klein[1,2,3], Matthew A. Stoodley[1,2], Luke A. Rochford[1,6], Joel Deyerling[4], David Hopkinson[1], Fulden Eratam[1], Tien-Lin Lee[1], Sam Sullivan-Allsop[7], Sarah J. Haigh[7], Roman Gorbachev[7], Christopher Allen[1,5], Wilhelm Auwärter[4], Reinhard J. Maurer[2], and David A. Duncan[1] — [1]Diamond Light Source, Didcot, UK — [2]University of Warwick, Coventry, UK — [3]Korea Basic Science Institute, Daejeon, ROK — [4]Technical University Munich, Germany — [5]University of Oxford, UK — [6]University of Cambridge, UK — [7]University of Manchester, UK

Introducing defects into graphene often requires post processing, like ion sputtering or plasma etching. We present a bottom-up synthesis method yielding graphene with incorporated topological defects on a copper substrate. In the chemical vapour deposition process we use an aromatic precursor that contains the same structural elements as the desired defect. During the growth of the graphene lattice, the topology of the precursor is partly retained and topological defects are formed in the carbonaceous network. In addition to the spectroscopic characterisation presented in the separate companion talk, we quantified the defect concentration using the direct imaging techniques of nc-AFM and TEM. Our results show that the ratio of ideal to defective graphene can be controlled by varying the substrate temperature during the growth process.

O 90.7 Thu 16:30 MA 005

Spectroscopic study of topological defects in graphene grown by bottom-up synthesis — Benedikt P Klein[1,2], Matthew A. Stoodley[1,2], Luke A. Rochford[1], Dylan B. Morgan[2], Michael Clarke[3], Alexander Generalov[4], Alexei Preobrajenski[4], Leon B. S. Williams[1], Tien-Lin Lee[1], Alex Saywell[3], Reinhard J. Maurer[2], and •David A. Duncan[1] — [1]Diamond Light Source, Didcot, UK — [2]University of Warwick, Coventry, UK — [3]University of Nottingham, UK — [4]MAX IV, Lund, Sweden

Introducing defects into graphene often requires post-processing, e.g. by ion sputtering or plasma etching. We present a bottom-up synthesis method yielding graphene with incorporated topological defects on a copper substrate. In the chemical vapour deposition process we use an aromatic precursor that contains the same structural elements as the desired defect. During the growth of the graphene lattice, the topology of the precursor is partly retained and topological defects are formed in the carbonaceous network. In addition to the direct imaging presented in the separate companion talk, we spectroscopically studied the defective graphene using the techniques of normal incidence X-ray standing waves (NIXSW), near edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) to elucidate the structural and chemical changes induced by varying defect concentration. Structurally, our results indicate that the adsorption height varies inversely with the defect concentration.

O 90.8 Thu 16:45 MA 005

Operando Characterization and Molecular Simulations Reveal the Growth Kinetics of Graphene on Liquid Copper — Valentina Rein[2], •Hao Gao[1], Hendrik H. Heenen[1], Oleg V. Konovalov[2], Karsten Reuter[1], and Maciej Jankowski[2] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]ESRF, Grenoble, France

In recent years, liquid metal catalysts have emerged as a compelling choice for the controllable, large-scale, and high-quality synthesis of two-dimensional materials. At present, there is little mechanistic understanding of the intricate catalytic process and its governing factors. In a combined experimental and computational study, we investigate the kinetics of graphene growth during chemical vapor deposition on a liquid copper catalyst. By monitoring the growing graphene flakes in real time using in situ optical microscopy, we explore the growth morphology and kinetics over a wide range of CH_4-to-H_2 pressure ratios and deposition temperatures. Constant growth rates of the flakes' radius indicate a growth mode limited by precursor attachment, whereas methane-flux-dependent flake shapes point to limited precursor availability. Large-scale free energy simulations enabled by an efficient machine-learning potential trained to density-functional theory data provide quantitative barriers for key atomic-scale growth processes. The experimental and theoretical data can be consistently combined into a microkinetic model that reveals a mixed growth kinetics that is controlled by both precursor availability and attachment. Key mechanistic aspects that explain improved graphene quality are a largely suppressed carbon dimer attachment and a self-healing mechanism.

O 90.9 Thu 17:00 MA 005

Structural and electronic properties of two-dimensional single-layer HfS_2 on Au(111) — •Monika Schied[1], Paolo Lacovig[1], Marco Bianchi[2], Philip Hofmann[2], and Silvano Lizzit[1] — [1]Elettra Sincrotrone Trieste — [2]Department of Physics and Astronomy, Aarhus University

HfS_2 is a promising 2D material for low-power semiconductor devices due to its predicted high electron mobility and low contact resistance for n-type carrier transport. For actual applications, layers with excellent structural and electronic properties are needed. However, films with the necessary quality are only available from exfoliation, which is neither scalable nor very reproducible and only few experimental studies on a single-layer (SL) of HfS_2 have been performed so far. In analogy to the growth of high-quality SL transition metal dichalcogenides such as MoS_2 and WS_2 [1,2] we have epitaxially grown an ordered layer of HfS_2 on Au(111). Monitoring the S 2p and Hf 4f core levels in real time by fast X-ray photoelectron spectroscopy allows the fine-tuning of the relevant parameters – such as the dosing rate and temperature – during the growth. The characterization by X-ray photoelectron diffraction, scanning tunnelling microscopy, and low-energy electron diffraction gives insight into the crystal structure of the film grown in this way. In addition, the electronic structure is investigated by angle-resolved photoemission spectroscopy.

[1] Bana, H., et.al., 2D Mater. 5 035012 (2018)
[2] Bignardi, L. et.al., Phys. Rev. Mat. 3, 014003, (2019)

O 90.10 Thu 17:15 MA 005

Na-doped Borophene/Ir(111) — •Sena Tömekce, Marc G. Cuxart, Knud Seufert, and Willi Auwärter — Physics Department E20, TUM School of Natural Sciences, Technical University of Munich, Garching, Germany

Alkali metal doping has been shown to be an effective strategy to tune the electronic properties of 2D materials, due to their low ionization energy [1,2]. Borophenes, 2D layers of covalently bonded boron atoms, combine many interesting properties such as polymorphism, anisotropy and metallicity, making them promising for various applications [3]. Particularly, when doped by alkali metals, free-standing borophenes have been predicted to be excellent materials for Li/Na ion batteries, offering high charge storage capacity, low diffusion barrier and maintaining metallic conductivity [4,5]. Here, we report on the high-resolution LT-STM (low temperature scanning tunneling microscopy) and XPS (X-ray photoelectron spectroscopy) characterization of Na-doped $\chi 6$ borophene/Ir(111). We demonstrate that Na atoms adsorb on borophene without forming clusters, after room temperature deposition. The Na adsorption sites on the borophene lattice were investigated. XPS reveals a binding energy shift of the B 1s core level upon increasing Na coverage, implying charge transfer.
[1] J. Cai et al., Phys. Rev. B. 2018, 98, 195443
[2] D. Marchiani et al., Nano Lett. 2023, 23, 170-176
[3] A. J. Mannix et al., Nat. Nanotechnology. 2018, 13, 444-450
[4] X. Zhang et al., Nanoscale. 2016, 8, 15340-15347
[5] J. Li et al., J. Electrochem. Soc. 2020, 167, 090527

O 90.11 Thu 17:30 MA 005

A buckled honeycomb lattice of Fe atoms grown on a clean Be(0001) surface — •Stefan Krause, Hermann Osterhage, Karoline Oetker, Radek Dao, and Roland Wiesendanger — Department of Physics, University of Hamburg, Germany

The Be(0001) surface is considered to be an ideal model system to host a 2D electron gas with pronounced electron-electron and electron-phonon interactions that are decoupled from the bulk [1,2]. Consequently, growing magnetic adlayers on Be(0001) raises expectations for the emergence of novel electronic and magnetic phases that result from the interactions between the 2D electron gas and the magnetic atoms. Here we report on our experimental studies of the epitaxial growth of Fe on a clean Be(0001) surface using scanning tunneling microscopy at low temperature. Individual Fe atoms are found to replace Be atoms in the topmost Be(0001) surface layer, driven by an atomic exchange. Increasing the Fe coverage results in the self-terminated growth of ultrathin films consisting of atomically well-ordered patches with a p(2×2) superstructure. Based on the atomic structure of the $FeBe_2$ bulk alloy we develop an atomistic growth model, where the dosing of Fe transforms the topmost Be layer into a Kagome lattice that supports the formation of a 2D buckled honeycomb lattice of Fe atoms. The experimental results will be presented and discussed in terms of the atomic lattice structure and spectroscopic characteristics in comparison with the clean Be(0001) surface.
[1] P. T. Sprunger *et al.*, Science **275**, 1764 (1997).
[2] H.Osterhage *et al.*, Phys. Rev. B **103**, 155428 (2021).

O 90.12 Thu 17:45 MA 005

Growth and structure of Chromium sulfide: a new magnetic 2D material — •Affan Safeer[1], Mahdi Ghorbani Asl[2], Wouter Jolie[1], Hannu Pekka Komsa[3], Arkady V. Krasheninnikov[2], Thomas Michely[1], and Jeison Fischer[1] — [1]Universität zu Köln, Köln, Germany — [2]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany — [3]University of Oulu, Oulu, Finland

We combine scanning tunneling microscopy (STM), low-energy electrons diffraction (LEED) and density functional theory (DFT) calculations to investigate growth, structure and properties of chromium sulfides fabricated by molecular beam epitaxy on graphene. The thinnest chromium sulfide formed has threefold symmetry, an in-plane lattice parameter of 0.340 +/- 0.002 nm, apparent STM height of 0.78-0.87 nm, and 2 Cr atoms per unit cell. Upon annealing of the thinnest, phase pure layers, compounds with same symmetry and lattice parameter, but with increased height in steps of 0.24 nm are formed. In combination with DFT calculations we find a five-layer stack S-Cr-S-Cr-S, namely Cr2S3, to yield excellent agreement with the experimental observations. Systematic variation of the stacking sequence in the DFT calculations of five- layer stacks makes plain, that Cr2S3 grows in the NiAs-structure. Thicker layer, as observed after annealing, are formed by covalent growth of multiples of additional CrS layers. Spin-polarized STM of Cr2S3 at 1.7 K displays hysteresis of the differential conductance signal as a function of out-of-plane magnetic field. This hysteresis is consistent with a ferromagnetic response of the top Cr-layer and antiferromagnetic alignment between Cr layers in Cr2S3.