

## O 117: Graphene II: Adsorption, Intercalation and Doping (joint session O/TT)

Time: Friday 10:30–12:30

Location: GER 37

O 117.1 Fri 10:30 GER 37

**Ab initio thermodynamics of hydrocarbons relevant to graphene growth at solid and liquid Cu surfaces** — ●MIE ANDERSEN, JUAN SANTIAGO CINGOLANI, and KARSTEN REUTER — Theoretical Chemistry, Technische Universität München, Germany

High quality graphene can be synthesized through chemical vapor deposition (CVD) at liquid Cu [1]. However, the role of the liquid catalyst surface is not yet well understood, and the role of hydrogen in the reactant mixture is still debated [2]. Here [3], we use *ab initio* thermodynamics to study the stability of a wide range of hydrocarbons under various CVD conditions (temperature, methane and hydrogen pressures) used in experimental growth protocols at solid and liquid Cu surfaces. We compare various low-index Cu facets and make use of hindered translator/rotator or ideal 2D gas models [4] to describe the adsorbate free energies. We find that smaller hydrocarbons will completely dehydrogenate under most CVD conditions. For larger graphene-like clusters, metal-terminated and hydrogen-terminated edges have very similar stabilities. While both cluster types might thus form during the experiment, we show that the low binding strength of clusters with hydrogen-terminated edges could result in instability towards desorption.

[1] D. Geng *et al.*, PNAS **109**, 7992 (2012)

[2] X. Zhang *et al.*, JACS **136**, 3040 (2014)

[3] M. Andersen, J.S. Cingolani, K. Reuter, J. Phys. Chem. C **123**, 22299 (2019)

[4] L.H. Sprowl *et al.*, J. Phys. Chem. C **120**, 9719 (2016)

O 117.2 Fri 10:45 GER 37

**Graphene on liquid Cu, a multiscale model rationalizing mesoscale flake alignment** — ●JUAN SANTIAGO CINGOLANI, KARSTEN REUTER, and MIE ANDERSEN — Chair of Theoretical Chemistry, Technical University of Munich, Germany

In recent years the use of liquid Cu as a catalyst during chemical vapor deposition (CVD) has emerged as a promising method for the continuous production of high-quality single layer graphene. The processes involved, such as carbon nucleation, defect healing, or flake alignment, remain largely unexplored or lack convincing atomic-scale rationalization. Of particular interest is the reported meso-scale interaction between growing flakes that leads to an ordering into 2D lattices.

To address the latter, we engage in a multiscale modeling study, hierarchically combining molecular dynamics (MD) simulations with continuum theory. Using a third-generation charge optimized many body potential (COMB3), the MD simulations reveal a strong interaction of graphene flakes with the liquid substrate, leading even to their partial immersion. On the basis of thus determined material parameters like surface energy, charge transfer or average flake height above the surface, we then set up a simple continuum model assuming the flakes to be spherically charged particles. Within an order of magnitude, this model rationalizes the experimental observation of a coalescence of the growing hexagonal flakes into a close-packed structure with well-defined inter-flake separation in terms of long-range capillary and electrostatic interactions.

O 117.3 Fri 11:00 GER 37

**Experimental access to thermodynamics and kinetics predicting the CVD growth of graphene on Cu** — ●PAUL LEIDINGER, JÜRGEN KRAUS, and SEBASTIAN GÜNTHER — TUM, Dept. Chemie, Lichtenbergstr. 4, D-85748 Garching

Most Graphene growth recipes by chemical vapor deposition (CVD) on copper in a reactive CH<sub>4</sub>/H<sub>2</sub> atmosphere are results of parameter variations optimized by trial and error. Many existing growth models described in the literature are qualitative or contain phenomenological parameters to describe the growth process. In our study, we aim at analyzing the key processes during CVD at 900-1050 °C while maintaining the defined geometry of a growing graphene flake surrounded by graphene free copper. For this purpose, it is essential to control the flake nucleation before and, more importantly, during the entire CVD growth. Systematic variation of the CVD parameters provides the experimental data used to formulate a kinetic model which predicts the graphene growth velocity as function of the chosen mass action constant Q. Determining experimentally the thermodynamic equilibrium of the CH<sub>4</sub> decomposition reaction enables us to use the equilibrium as

reference point to which any chosen CVD parameter set can be related quantitatively. With experimental validation of our growth model we can understand both, the thermodynamics and kinetics of graphene growth on copper. Furthermore, we can also predict the growth rate of single graphene flakes formed during any CVD experiment on copper at high precision.

O 117.4 Fri 11:15 GER 37

**Stacking Relations and Substrate Interaction of Graphene on Copper Foil** — ●PHILIP SCHÄDLICH<sup>1</sup>, FLORIAN SPECK<sup>1</sup>, STIVEN FORTI<sup>2</sup>, CAMILLA COLETTI<sup>2</sup>, and THOMAS SEYLLER<sup>1</sup> — <sup>1</sup>Technische Universität Chemnitz, Chemnitz, Germany — <sup>2</sup>Istituto Italiano di Tecnologia, Pisa, Italy

Graphene-based device production requires graphene sheets of perfect crystallinity and low defect density on a large scale. Beyond mechanical exfoliation, where the flake size is uncontrollable, there are two promising approaches for high-quality wafer-scale graphene growth: (i) the sublimation growth on silicon carbide (SiC) by thermal decomposition of the substrate [1] and (ii) the chemical vapour deposition (CVD) on metal substrates such as copper [2].

In the present study we investigate the crystallinity of CVD grown graphene and the orientation with respect to the underlying copper foil by means of low-energy electron microscopy (LEEM) and diffraction (LEED). We find a lattice match within  $\pm 1^\circ$  between the graphene and the Cu(111) surface, which shows a surface faceting depending on the graphene thickness on top. Recently, stress-induced stacking domains in bi- and multilayer graphene were found for epitaxial graphene on SiC [3], revealing a much less homogeneous system than believed. Our LEEM dark field images and reflectivity spectra suggest a similar decomposition into domains of different stacking order for the CVD grown graphene flakes. [1] K. V. Emtsev *et al.*, Nature Mater. **8**, 203 (2009). [2] X. S. Li *et al.*, Science **324**, 1312 (2009). [3] T. A. de Jong *et al.*, Physical Review Materials **2**, 104005 (2018).

O 117.5 Fri 11:30 GER 37

**Sidewall epigraphene investigated by STEM** — ●MARKUS GRUSCHWITZ, STEFFEN SCHULZE, and CHRISTOPH TEGENKAMP — TU Chemnitz, Chemnitz, Germany

Epitaxial graphene nanoribbons (GNR) grown on SiC facets reveal ballistical transport channels. The structure and growth were studied intensively by STM, LEED and LEEM [1]. Spatially resolved transport measurements and tight-binding calculations suggest that the bonding of the ribbons to the SiC substrate plays an important role [2]. In this study, cross-section STEM on similar structures were performed in order to characterize the interface and bonding between graphene and SiC in more detail.

Indeed, the zig-zag GNRs, grown along the [1100] direction, are delaminated from the SiC facet as seen by high resolution C<sub>S</sub> corrected STEM. Mini steps at the top and the bottom of the sidewalls define the edges of the GNRs. Atomically resolved EELS and EDX confirm that the top part of the freestanding GNR merges into a bufferlayer. The SiC facet reveals a silicon deficiency in the three topmost substrate layers. These SiC imperfections were found already for epitaxial graphene on SiC(0001) and result from the sublimation processes [3]. The lower edge merges into SiC and shows a sp<sup>3</sup>-hybridization. Moreover, differential phase contrast measurements allow the calculation of charge density maps and therefore the visualization of space charge distributions in the substrate. References: [1] Zakharov *et al.*, ACS Appl Nano Mat., **2**, 156 (2019) [2] Aprojanz *et al.*, Nat. Comm. **9**, 4426, (2018). [3] Gruschwitz *et al.*, PRM **3**, 094004 (2019).

O 117.6 Fri 11:45 GER 37

**Epitaxial growth of high-quality armchair graphene nanoribbons** — ●H. KARAKACHIAN<sup>1</sup>, J. APROJANZ<sup>2</sup>, T. T. N. NGUYEN<sup>2</sup>, A. A. ZAKHAROV<sup>3</sup>, R. YAKIMOVA<sup>4</sup>, P. ROSENZWEIG<sup>1</sup>, C. M. POLLEY<sup>3</sup>, T. BALASUBRAMANIAN<sup>3</sup>, C. TEGENKAMP<sup>2</sup>, and U. STARKE<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Festkörperforschung, Stuttgart — <sup>2</sup>Institut für Physik, Technische Universität Chemnitz — <sup>3</sup>MAX IV laboratory, Lund — <sup>4</sup>IFM, Linköping University

Graphene nanoribbons (GNRs) are considered to be the fundamental building blocks for future carbon-based nanoelectronics. The functionality of GNRs is governed by the detailed atomic structure of

their edges. Namely, a GNR terminated by armchair edges develops a bandgap in its electronic structure driven by quantum confinement effects, where the size of the bandgap scales with the width of the ribbon itself. Thus, the controlled growth of armchair GNRs (AC-GNRs) may solve the long-lasting problem of graphene, which is its inability to be embedded in modern quantum integrated circuitry. Here, we grow high-quality AC-GNRs on the sidewalls of 6H-SiC mesa structures. Using angle-resolved photoelectron spectroscopy we study the electronic structure of the one-dimensionally (1D) confined AC-GNRs which truly reveals a width-dependent bandgap formation. We observe a set of well-resolved sub-bands and a Fermi surface that consists strictly of a straight line which are characteristic features of 1D confined systems. Our findings provide a solid ground for further theoretical assessment and a deeper understanding of quantum confinement phenomena.

O 117.7 Fri 12:00 GER 37

**Monodispersed graphene nanoribbons on Ag(111) by electropray controlled ion beam deposition: their self-assembly and on-surface extension visited by STM** — ●WEI RAN<sup>1</sup>, ANDREAS WALZ<sup>1</sup>, KAROLINA STOIBER<sup>1</sup>, PETER KNECHT<sup>1</sup>, ANTHOULA C. PAPAGEORGIOU<sup>1</sup>, ANNETTE HUETTIG<sup>1</sup>, DIEGO CORTIZO-LACALLE<sup>2</sup>, JUAN P. MORA-FUENTES<sup>2</sup>, AURELIO MATEO-ALONSO<sup>2,3</sup>, HARTMUT SCHLICHTING<sup>1</sup>, JOACHIM REICHERT<sup>1</sup>, and JOHANNES V. BARTH<sup>1</sup> — <sup>1</sup>Physics Department E20, Technical University of Munich, Germany — <sup>2</sup>POLYMAT, University of the Basque Country UPV/EHU, Spain — <sup>3</sup>Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Graphene nanoribbons (GNRs) are of interest due to their potential in electronics, energy conversion, and storage. For atomically precise GNRs, elaborate bottom-up fabrication protocols have been developed, utilising the reactivity of a metallic support.<sup>1</sup> However this approach often results in GNR arrays with a variety of lengths. Here we employ

a different approach for the preparation and study of GNRs on surfaces: chemical synthesis and purification of well-defined nanoribbons<sup>2</sup> followed by processing with electropray controlled ion beam deposition (ES-CIBD). With this method, we can deposit well-defined GNRs on any solid support under ultra-high vacuum conditions. The quality of the films produced is exemplified for a  $\sim 3$  nm GNR on Ag(111). We explore their self-assembly and thermally activated polymerisation reactions by means of scanning tunnelling microscopy.

- 1) Fasel et al. *Adv. Mater.* **2016**, *28*, 6222.
- 2) Mateo-Alonso et al. *Angew. Chem., Int. Ed.* **2018**, *57*, 703.

O 117.8 Fri 12:15 GER 37

**Understanding trends in lithium binding at 2D materials** — ●ZELJKO SLJIVANCANIN<sup>1,2</sup>, SRDJAN STAVRIC<sup>2</sup>, and ZORAN S. POPOVIC<sup>2</sup> — <sup>1</sup>Serbian Academy of Sciences and Arts, Belgrade, Serbia — <sup>2</sup>Vinca Institute of Nuclear Sciences, Belgrade, Serbia

Employing density functional theory we studied microscopic mechanisms governing binding of metal atoms and their nanostructures at selected 2D materials. We considered the interaction of a Li adatom with monolayers of several transition metal oxides and dichalcogenides, carbides of group XIV elements, functionalized graphene, silicene and germanene, as well as black phosphorus and Ti<sub>2</sub>C MXene. We found that the general trend in Li binding can be estimated from positions of conduction band minima of 2D materials, since the the energy of the lowest empty electronic states shows a nice correlation with the strength of Li adsorption [1]. At variance to the majority of studied surfaces where occurs a simple electron transfer from Li to the substrate, in monolayers of carbides of group XIV elements Li adsorbates profoundly modify substrates, creating well-localized mid-gap states. This gives rise to their capability to accommodate Li structures with the nearly constant binding energy of alkaline atoms over Li coverages ranging from well-separated adatoms to a full monolayer.