

CPP 16: Nanostructures at Surfaces (joint session O/CPP)

Time: Monday 15:00–17:45

Location: GER 39

CPP 16.1 Mon 15:00 GER 39

Tailoring Stone-Wales transitions in Ti_2O_3 honeycombs with alkaline earth metals — ●MARTIN HALLER, STEFAN FÖRSTER, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Institute of Physics, Von-Danckelmann-Platz 3, 06120 Halle, Germany

In 2013 the first 2D oxide quasicrystal (OQC) has been discovered in thin Ba-Ti-O films [1]. It shows a twelfold diffraction pattern that is incompatible with lattice periodicity. In real space it can be described by squares, triangles and rhombus tiles. Just recently, the atomic structure has been solved [2,3]. The essence are Ti_nO_n ring structures with $n = 4, 7$ and 10 . These evolve by Stone-Wales transitions from a pure honeycomb network [4]. The transformations are stabilized by alkaline earth metal ions and their associated dipole and can be controlled by the alkaline earth metal coverage. Here we investigate the basic steps of individual Stone-Wales transformations with LEED and STM for ultra-low coverages deposited onto a Ti_2O_3 honeycomb on a close-packed metal surface. The transformations to ring structures with $n = 4, 5$ and 7 are monitored and related to the formation of square and triangle tilings.

[1] S. Förster et al., *Nature* 502, 215 (2013)

[2] S. Schenk et al., *Nat. Comm.*, accepted, (2022)

[3] E. Cockayne et al., *Phys. Rev. B* 93, 020101 (2016)

[4] S. Wang et al., *Nanoscale* 11, 2412 (2019)

CPP 16.2 Mon 15:15 GER 39

Formation of an extended quantum dot array driven and auto protected by an atom thick h -BN layer — ●JOEL DEYERLING¹, IGNACIO PIQUERO-ZULAICA¹, MUSTAFA A. ASHOUSH², KNUD SEUFERT¹, MOHAMMAD A. KHER-ELDEN², ZAKARIA M. ABD EL-FATTAH², and WILLI AUWÄRTER¹ — ¹Physics Department E20, Technical University of Munich, James-Frank-Straße 1, D-85748 Garching, Germany — ²Physics Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo E-11884, Egypt

Fabricating nanoarchitectures to confine two dimensional nearly free electrons on crystalline surfaces by tip manipulation with a scanning tunneling microscope (STM) or by applying supramolecular chemistry principles yields diverse artificial electronic structures. These electronic states are prone to scattering by adsorbates making them extremely susceptible to the environment. Nonetheless, little attention has been given to their protection, e.g., by an inert overlayer.

Here, we show that a quasi-hexagonal CuS nanoporous network can be formed at the h -BN/Cu(111) interface by thermally-induced sulfur segregation from the Cu(111) bulk. The growth and structure is characterized by STM and X-ray photoemission spectroscopy. We demonstrate by employing STM and scanning tunneling spectroscopy that within the pores of the network the surface state of Cu(111) as well as the image potential states of h -BN/Cu(111) are confined, effectively creating arrays of quantum dots with well-defined sizes that are covered by an inert h -BN overlayer.

CPP 16.3 Mon 15:30 GER 39

First-principles investigation of doped borophene quantum dots as donor materials for solar cell applications — ●RACHANA YOGI, VAISHALI ROONDHE, and ALOK SHUKLA — Department of Physics, Indian Institute of Technology Bombay, Mumbai 400076, India

Because of fast-depleting fossil fuel reserves, there is an urgent need for harvesting alternative sources of energy. We present a first-principles atomistic study of borophene quantum dots (BQDs) B35 and B36 for their possible utilization in solar-cells. The pristine-BQDs are doped by C, N, and O atoms, and find that they have bowl-like structures in the ground state. The electronic and optical properties of pristine-BQDs, and doped-BQDs are investigated. The chemical potentials of several of these BQDs are slightly higher than that of popular solar-cell acceptor system PC71BM, they will act as electron donors in a PC71BM-based solar-cell. The calculated values of the open-circuit voltage corresponding to PC71BM and BQD-based device indicate efficient electron injection from the BQDs to PC71BM. O-doped B36-QD and B35-QD have the highest value of short-circuit current density attributed to their reduced HOMO-LUMO gap and high HOMO energy levels as compared to all other considered doped systems further enhancing the photoelectric properties. The power conversion efficiency

of doped-BQDs exhibits significant improvement. The efficiency of O-doped B36-QD is maximum due to its high electron injection rate in PC71BM. Present calculations show that adding a foreign atom in BQD makes it a suitable candidate for high-performance solar-cells.

CPP 16.4 Mon 15:45 GER 39

Electrospray Depositions of a Spin-Crossover Active Iron(II) $[2 \times 2]$ Grid Complex on Ag(111) with Different Landing Energies — ●DENNIS MEIER¹, BENEDIKT SCHOOP¹, JOACHIM REICHERT¹, NITHIN SURAYADEVARA², ANDREAS WALZ¹, ANNETTE HUETTIG¹, HARTMUT SCHLICHTING¹, MARIO RUBEN², ANTHOULA C. PAPAGEORGIOU^{1,3}, and JOHANNES V. BARTH¹ — ¹Technical University of Munich, Germany — ²Karlsruhe Institute of Technology, Germany — ³National and Kapodistrian University of Athens, Greece

Chiral spin-crossover (SCO) complexes are intriguing building blocks for innovative magneto-optical nanoarchitectures.¹ Such an Fe(II) $[2 \times 2]$ grid complex was deposited in ultra-high vacuum with electrospray controlled ion beam deposition (ES-CIBD)² on Ag(111) and investigated by scanning tunnelling microscopy. Low landing energy (< 3 eV/z) resulted in clusters and single molecules. Higher landing energies (> 3 eV/z) led to coordination bond cleavage and a rich variety of self-assembled surface networks forming from the grid fragments. Applying established on-surface synthesis methodology employing the possible constituents of these networks (ligands and Fe atoms) reproduced only a part of them. It is thus proposed that ES-CIBD provides an unexpected route to novel on-surface coordination network synthesis.

[1] N. Suryadevara et al. *Chem. Eur. J.* 2021, **27**, 15172.

[2] A. Walz, K. Stoiber, A. Huettig, H. Schlichting, J. V. Barth, *Anal. Chem.* 2022, **94**, 7767.

CPP 16.5 Mon 16:00 GER 39

Giant confinement of surface electrons in a two-dimensional metal-organic porous network — ●LU LYU¹, TOBIAS EUL¹, WEI YAO¹, ZAKARIA M. ABD EL-FATTAH², MOSTAFA ASHOUSH², IGNACIO PIQUERO-ZULAICA³, JOHANNES V. BARTH³, MARTIN AESCHLIMANN¹, and BENJAMIN STADTMÜLLER^{1,4} — ¹Department of Physics, University of Kaiserslautern, Germany. — ²Physics Department, Faculty of Science, Al-Azhar University, Egypt. — ³Physics Department E20, Technical University of Munich, Germany — ⁴Institute of Physics, Johannes Gutenberg University Mainz, Germany.

Two-dimensional metal-organic porous networks (2D-MOPNs) are highly flexible nano-architectures for exploring the quantum confinement of surface electrons on noble metals. So far, 2D-MOPNs have been predominantly studied for the confinement of occupied Shockley-type surface states (SS). In contrast, the confinement of excited surface states, such as image potential states (IPs), remains elusive. In this work, we apply two-photon photoemission to investigate the band dispersion of the first image-potential state ($n = 1$ IPS) in a Cu-T4PT nanoporous network on Cu(111). We find the formation of a Bloch-like band structure with a substantially increased effective band mass of the IPS ($> 150\%$). In contrast, the effective band mass of the SS remains almost unchanged ($< 3\%$). This band renormalization of the IPS can be attributed to the spatial distribution of its charge density perpendicular to the surface, which reveals the highest density at the vertical adsorption position of the T4PT backbone. This coincidence is responsible for the giant confinement.

CPP 16.6 Mon 16:15 GER 39

Modification of Single-Layer Organometallic Networks: from Ag-Bridged to Cu-Bridged Alkynyl Metal-Alkynyl Linkages on Ag(111) Surfaces — ●WENCHAO ZHAO, FELIX HAAG, IGNACIO PIQUERO-ZULAICA, YI-QI ZHANG, FRANCESCO ALLEGRETTI, BIAO YANG, and JOHANNES V BARTH — Physics Department E20, Technical University of Munich, 85748 Garching, Germany

The metal-exchange reaction, is of importance for the advanced preparation of functional metal-organic frameworks for various applications[1]. Notably, building two-dimensional organometallic networks (OMNs), can provide versatile nanoarchitectures for potential application in nanodevice[2,3]. Although various OMNs have been constructed with molecular building blocks by abstracting surface metal atoms, the degree of success is often individual and substrate-

dependent. Thus metal-exchange reactions hold promise for multiple production by modification and functionalization of OMN templates. Here, we demonstrate the modification of a single-layer OMN by metal-exchange reaction. By introducing external Cu atoms into the alkynyl-Ag OMN[3], we successfully synthesized in situ a highly ordered alkynyl-Cu OMN on a Ag(111) surface. While maintaining a similar lattice periodicity and pore morphology, it possesses higher thermal stability, guaranteeing higher robustness for possible applications. Reference. 1. M.-M. Xu et al., *Coord. Chem. Rev.* 2020, 421, 213421. 2. D. Ecija et al., *Acc. Chem. Res.* 2018, 51, 365-375. 3. Y.-Q. Zhang et al., *J. Am. Chem. Soc.* 2019, 141, 5087-5091

CPP 16.7 Mon 16:30 GER 39

Structure Formation in Ceramic Thin Films with Hybrid Molecular Dynamics — ●NYDIA ROXANA VARELA ROSALES and MICHAEL ENGEL — Institute for Multiscale Simulation, University of Erlangen-Nürnberg, Cauerstraße 3, 91058 Erlangen, Germany

How can we model and predict ceramic thin films? Highest accuracy is achieved with ab-initio quantum mechanical methods. But these methods are not suitable for large systems including their phase transformations. Atomistic modeling with molecular dynamics and Monte Carlo simulations reaches large system sizes but require sophisticated tailored interaction potentials. Here, we develop and apply a coarse-grained simulation method for structure formation in thin films. Our method considers the chemical bond network of the ceramics explicitly to simplify the complexity of the simulation and to reach high simulation speeds and large system sizes. Of particular interest are (quasi-)crystalline ceramic thin films recently discovered in experiments of (Ba/Sr)-Ti-O perovskites. Solely by considering the extrinsic topology of the tiles and utilizing a harmonic interaction potential, we reproduce the appearance of approximants of the dodecagonal quasicrystals, which was also predicted by ab-initio simulations. Our work highlights the role of bond network topology in understanding complex thin film structures without a need for reliance on quantum simulation methods.

CPP 16.8 Mon 16:45 GER 39

A Holistic Characterisation of Bi Thin Films on Au(111) — ●PABLO VEZZONI VICENTE¹, TOBIAS WEISS¹, MARC GONZALEZ-CUIXART⁴, DENNIS MEIER¹, BENEDIKT KLEIN², DAVID DUNCAN², EZEQUIEL TOSI³, PAOLO LACOVIG³, SILVANO LIZZIT³, JOHANNES BARTH¹, PETER FEULNER¹, and FRANCESCO ALLEGRETTI¹ — ¹Physics Department E20, Technische Universität München, Germany — ²I09 beamline, Diamond Light Source, United Kingdom — ³SuperESCA beamline, Elettra Synchrotron, Italy — ⁴IMDEA Nanociencia, Spain

We present a comprehensive analysis of the long-range ordered, coverage-dependent phases of Bi epitaxially grown on a Au(111) surface in UHV, from the sub-monolayer ($\sqrt{37} \times \sqrt{37}$)R25.3° Kagome lattice up to few-layer Bi(110) thin films. Particular focus is devoted to the sub-monolayer, high-coverage ($p \times \sqrt{3}$) phase, paving the way to its use as a buffer layer for epitaxial growth with tunable geometry and low electronic interaction.

Our work clarifies and expands the current literature reports, specifically on the complex ($p \times \sqrt{3}$) phase. The wide range of analysis techniques used, including Low-Energy Electron Diffraction (LEED), Photo-Electron Spectroscopy (XPS, UPS), Temperature Programmed Desorption (TPD), Scanning Tunneling Microscopy and Spectroscopy (STM, STS), and X-ray Standing Waves (XSW), yields an unprecedented understanding of the system's structural and electronic properties.

CPP 16.9 Mon 17:00 GER 39

Analytical electron microscopy of nanostructured vanadium dioxide — ●VLASTIMIL KRÁPEK¹, JAN KRPEŇSKÝ^{1,2}, MICHAL HORÁK¹, KATARÍNA ROVENSKÁ¹, PETER KEPIČ¹, TOMÁŠ ŠIKOLA¹, FILIP LIGMAJER¹, and ANDREA KONEČNÁ¹ — ¹Brno University of Technology, Czechia — ²CIC nanoGUNE, San Sebastián, Spain

Vanadium dioxide (VO₂) is a phase-changing material exhibiting

temperature-induced metal-insulator transition (MIT) around 340 K. A rather low transition temperature makes VO₂ a suitable material for active nanophotonics, e.g., switchable optical metasurfaces. Such applications require nanostructuring of VO₂ thin films. Here we study the possibility to employ focused ion beam (FIB) milling for the nanofabrication and its impact on the properties of resulting nanostructures.

Taking the VO₂ thin film with experimentally verified MIT, we utilized FIB milling with Ga ions to fabricate V-shaped lamella of the thickness between 0 and 250 nm, which was subsequently transferred onto a heating chip for transmission electron microscopy and analyzed with analytical electron microscopy: high-resolution imaging, energy-dispersive X-ray spectroscopy, and temperature-dependent electron energy loss spectroscopy. We observed a porous character of the pristine material, a coexistence of several crystal structures, negligible contamination with Ga ions, and a variation of stoichiometry with the thickness of the lamella, with the thinnest parts composed of VO and V₂O₃.

CPP 16.10 Mon 17:15 GER 39

Tuning Nanoporous Au Film Formation via High Voltage Electrolysis — ●EVELYN ARTMANN¹, LUKAS FORSCHNER¹, KONSTANTIN M. SCHÜTTLER², MOHAMMAD AL-SHAKRAN¹, TIMO JACOB¹, and ALBERT K. ENGSTFELD¹ — ¹Institute of Electrochemistry, University of Ulm, Germany — ²Institute of Surface Chemistry and Catalysis, University of Ulm, Germany

Nanoporous Au (NPG) films have different properties compared to the bulk material, which opens up new areas of application, such as (electro)catalysis. Usually, NPG films are prepared by dealloying. One disadvantage of this method is that residues of the precursor alloy guest metal can remain in the resulting NPG film, which can have a decisive influence on the electrocatalytic activity of the NPG film.

In this work we report on the preparation of NPG films by high voltage electrolysis (*Chem. Phys. Chem.*, 22 (2021) 2429). In this process, a Au oxide film is first formed on the Au substrate by applying a high positive voltage (between 100 and 540 V), which can subsequently be reduced to NPG. The Au oxide as well as NPG films were characterized by electrochemical methods, as well as (cross-section) SEM and XPS measurements.

Possibilities to selectively modify the resulting NPG films by tuning experimental parameters such as the applied voltage, and electrolyte temperature during HV electrolysis, or the electrolysis time, were systematically investigated. The influence of the reduction method (electrochemical or by H₂O₂) on the final film structure is discussed.

CPP 16.11 Mon 17:30 GER 39

Evolution of the Si-Au alloy: from the gold (110) substrate to silicon nanoribbons — ●EKATERINA TIKHODEEVA¹, MARÍA E DÁVILA², PAOLA DE PADOVA³, GAY LE LAY⁴, MARINA BAIDAKOVA⁵, EVGENIYA LOBANOVA⁵, JAIME SANCHEZ-BARRIGA⁶, DMITRII SMIRNOV⁶, and MANUEL IZQUIERDO¹ — ¹European XFEL, Schenefeld, Germany — ²CSIC, Madrid, Spain — ³Consiglio Nazionale delle Ricerche, Rome, Italy — ⁴Aix-Marseille Université, Marseille, France — ⁵Saint Petersburg, Russia — ⁶Helmholtz-Zentrum Berlin, Berlin, Germany

The development of the Si-Au alloy was investigated on the path from the gold single crystal surface to silicon nanoribbons (SiNR). Si sub-monolayers were deposited on the missing row reconstructed Au(110) substrate. At various stages of evaporation, low-energy electron diffraction (LEED) patterns were recorded to refine the surface geometry. The arrangement of the Si atoms has been correlated with the missing row orientation. The recovery of the Au(1x1) reconstruction, as well as the gradual transition from surface alloy to SiNRs were explored. In parallel with LEED, photoelectron spectroscopy was used to clarify the atom distribution. The profiles of the Au 4f and Si 2p core levels were deconvoluted and analyzed at all stages of Si deposition. The appearance of a new low kinetic energy component was noticed in the Au 4f spectra. It is related to the Si-Au bond and indicates a strong interaction between them. The Si core levels exhibit up to three components corresponding to the different chemical environments.