

O 48: Focus Session: Semiconductor Surface Chemistry – from Reaction Mechanisms to Well-Ordered Interfaces I

The interest in the properties of semiconductor surfaces and chemical reactions on these surfaces is driven by a large range of current and future applications. They are spanning from conventional microelectronics over molecular electronics, atomic scale and quantum devices to photo(-electro)-chemical processes for large-scale synthesis of chemicals such as hydrogen and ammonia. In this focus session, the wide variety of topics in semiconductor surface chemistry is illustrated in the same way as the common aspects of the field are emphasized. In particular, the question how to control the reactivity on semiconductor surfaces, which is typically governed by the high localization of charge at the surface dangling bonds, will be addressed for the different systems. A larger part of the session will be dedicated to the reaction of organic molecules on semiconductor surfaces and how the control of these reactions can lead to the synthesis of ordered organic architectures with well-controlled properties on semiconductor surfaces.

Organizer: Michael Dürr (U Giessen)

Time: Wednesday 10:30–12:15

Location: GER 38

Topical Talk

O 48.1 Wed 10:30 GER 38

Surface functionalization of semiconductors: Introducing spectroscopic labels, monolayer control for ultra-shallow doping, and providing surface passivation for atomically-precise processes — ●ANDREW TEPLYAKOV — 112 Lamont DuPont Laboratory, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

Over the last several decades, chemistry for surface functionalization of semiconductors went through a number of directional changes that were largely dictated by the technology development. Some of the recent work in our group has been targeting modification of both flat surfaces and the surfaces of nanoparticulate semiconductor materials to introduce spectroscopic labels, provide monolayer control for ultra-shallow doping, and also to control the passivation of surfaces for atomically-precise processes. This presentation will start with applying the basic principles of surface chemical design to silicon surfaces. Specifically, I will cover the solution reactions of boron- and nitrogen-containing compounds with hydrogen- and chlorine-terminated silicon surfaces. Parallels and major differences between the chemistry of (100) and (111) crystal faces of silicon will be examined. The reactions of the same surfaces with metalorganic precursor molecules will be presented to evaluate the role of minority sites (defects) in atomically-precise processing. Finally, the parallels between surface chemical modification of flat silicon surfaces and metal oxide nanomaterials will be examined and the challenges in connecting physical and chemical properties of these materials will be evaluated.

O 48.2 Wed 11:00 GER 38

Theoretical studies on surface stabilities of FeCuO₂ and CuBi₂O₄ — ●JULIAN BESSNER, STEFANIE BOGENRIEDER, BJÖRN KIRCHHOFF, and TIMO JACOB — Ulm University, Institute of Electrochemistry, D-89081 Ulm

Ammonia is the most important component in fertilizers, as 80% of the worldwide production goes into fertilizers.[1] Currently, the energetically expensive Haber-Bosch process is used to break the triple bond of N₂. In the last years, the photoelectrochemical (PEC) reduction of nitrogen has gained attention, providing a more affordable and sustainable ammonia production. To this end, CuFeO₂ and CuBi₂O₄ are investigated as materials for photocathodes as promising alternatives for the conversion of solar energy into chemical fuels.[2, 3] So far, most theoretical and experimental studies on these materials had focused on bulk properties. Here, we perform Density Functional Theory calculations (DFT+U) to analyze their electronic properties, thermodynamic stability of different surfaces and adsorption energy trends for the nitrogen reduction reaction (NRR) intermediates. Additionally, the influence of an aqueous surrounding on the stability of the surfaces and reaction intermediates thereon will be investigated using the hybrid QMMM simulation approach (SAFIRES) implemented in ASE and GPAW, which to this end will be extended to be compatible with periodic surface models.

[1] Smil, V. Nature 400, 1999, 415.

[2] Jiang, C.-M. et al. Chem. Mater., 31, 7, 2019, 2524-2534

[3] Ferri, M. et al. ACS Catalysis 11 (4), 2021, 1897-1910.

Topical Talk

O 48.3 Wed 11:15 GER 38

Growth of organic monolayers on Si(111) — ●MARTIN FRANZ — Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Germany

The ever-growing number of semiconductor based applications leads to an increasing demand for a modification or functionalization of surfaces with organic molecules. However, while the formation of self-assembled monolayers of organic molecules is well established on metal surfaces, the high density of dangling bonds present on most clean semiconductor surfaces typically reduces the mobility of molecules preventing an ordered growth. A route to overcome this constraint is the modification of the surface, allowing to precisely adjust the substrate-molecule interaction enabling a controlled growth.

In this talk, examples of organic films on modified Si(111) surfaces are given, which were investigated using scanning tunneling microscopy as well as tunneling and photoelectron spectroscopy. A prominent example in this regard is the boron-modified Si(111) $\sqrt{3} \times \sqrt{3}$ R30°-B surface. Here, results for N-heterocyclic carbenes, which form highly ordered monolayers with promising properties [1], and for cobalt phthalocyanine [2-3] are discussed. Further examples given include the influence of surface defects on the molecular adsorption process and the use of indium-modified Si(111) as substrate [4].

[1] M. Franz et al., Nat. Chem. **13**, 828 (2021).

[2] S. Lindner et al., Phys. Rev. B **100**, 245301 (2019).

[3] H. Aldahhak et al., Phys. Rev. B **103**, 035303 (2021).

[4] M. Kubicki et al., Appl. Phys. Lett. **119**, 133105 (2021).

O 48.4 Wed 11:45 GER 38

Organic molecular architectures synthesized by means of solution-based click chemistry on functionalized silicon surfaces — ●TIMO GLASER¹, JANNICK ALEXANDER PETERS¹, CHRISTIAN LÄNGER¹, DOMINIK SCHARF², JANNICK MEINECKE², ULRICH KOERT², and MICHAEL DÜRR¹ — ¹Institut für Angewandte Physik und Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany — ²Fachbereich Chemie, Philipps-Universität Marburg, Germany

The application of organic click chemistry to selectively functionalized silicon surfaces may open the route to synthesizing new organic molecular architectures on silicon. However, this scheme seems to be an experimental contradiction since click reactions are performed in the presence of a catalyst dissolved in a solvent whereas the highly reactive Si(001) surface is prepared and stored under UHV conditions. Here we show how to combine surface functionalization performed under UHV conditions with solution-based alkyne-azide click reactions. The UHV-based functionalization of Si(001) was realized via chemoselective adsorption of ethynyl cyclopropyl cyclooctyne (ECCO) from the gas phase. The samples were then directly transferred from UHV into the reaction solution where alternating layers of bisazide and bisalkyne were coupled subsequently step by step without exposure to ambient conditions. Each reaction step was monitored by means of XPS in UHV and the selectivity of the reaction schemes in use was demonstrated. Using optimized copper(I) catalysts, reaction yields of up to 75 % were obtained.

O 48.5 Wed 12:00 GER 38

Towards Ab Initio Design of Internal Interfaces - The Adsorp-

tion of Cyclooctyne on Semiconductor Surfaces — ●HENDRIK WEISKE and RALF TONNER-ZECH — Universität Leipzig, Germany

Modern Society is massively influenced by technological progress, specifically the development of the electronics industry. The controlled functionalization of semiconductor interfaces with organic molecules offers new possibilities to advance the application range of classical semiconductors. The chemoselective attachment of multifunctional organic molecules is the first step in forming well-defined organic/semiconductor interfaces.

Previously, we investigated the functionalization of Si(001) surfaces extensively [1,2]. This research focussed on bifunctional cyclooctyne,

which attaches to Si(001) via its strained triple bond. This work is extended here to various semiconducting substrates, such as Ge(001), to predict new and promising interfaces. The reactivity and fundamental bonding interactions are studied using various computational methods, such as the pEDA, AIMD, and NEB.

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References

- [1] F. Pieck, R. Tonner-Zech, *Molecules* **2021**, *26*, 6653
- [2] L. Pecher, S. Schmidt, R. Tonner, *J. Phys. Chem. C*, **2017**, *121*, 26840-26850