O 61: Semiconductor Surfaces: Adsorption and Reactivity

Time: Wednesday 15:00–17:30 Location: H25

O 61.1 Wed 15:00 H25

Atomic structure of As-modified Si(100) surfaces prepared in MOCVD ambient — •Agnieszka Paszuk[1], Oleksandr Romanyuk[2], Oliver Supplie[1], Manali Nandy[1], Peter Kleinschmidt[1], and Thomas Hannappel[1] — [1]Institute for Physics, University of Technology, Ilmenau, Germany — [2]Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

For highly efficient III-V-on-Si tandem solar cells it is crucial to avoid defects known as antiphase boundaries at the III-V/Si interface by preparing the Si(100) surface with double-layer (DL) steps. While preparation of the DL-stepped Si(100) surfaces in As-rich metalorganic chemical vapor deposition (MOCVD) ambience has been investigated, their surface structure is still not fully understood. Here, the DL-stepped Si(100) surfaces are prepared in As-rich MOCVD ambience and the entire process is monitored by optical *in situ* spectroscopy. The Si:As surfaces are investigated by surface-sensitive techniques in ultra-high vacuum. With scanning tunneling microscopy (STM), we observe different Si:As surface structures in dependence on the substrate miscut and preparation routes. The low-offcut Si(100):As surfaces exhibit evenly spaced, atomically flat terraces with a random distribution of darker and brighter areas, which stem from a different local electronic structure. STM scans of vicinal Si(100):As surfaces show zig-zag chains and asymmetrical protrusions. Density functional theory calculations predict that, in H_2 ambient, the commonly assumed As-As dimer termination on top of Si(100) is not energetically favorable and the surface structure strongly depends on the H and As chemical potentials.

O 61.2 Wed 15:15 H25

The impact of Al on defects introduced during GaP nucleation on Si(100) 2° substrate by MOCVD — •Manali Nandy, Agnieszka Paszuk, Christian Koppka, Oliver Supplie, Peter Kleinschmidt, and Thomas Hannappel — Institute for Physics, University of Technology, Ilmenau, Germany

The performance of III-V-on-Si multi-junction solar cells is still limited by a high density of defects at the GaP/Si heterointerface and in the III-V buffer. Here, the GaP buffers are grown on Si(100)2° substrates by metalorganic chemical vapor deposition in Al-free (as a reference) or in Al-containing reactors. In the latter one, Al was supplied either directly during the GaP nucleation from the TMAl precursor or indirectly from Al residuals present in the reactor from previous processes. Defects in the GaP buffers are investigated by electron channeling contrast imaging (ECCI). The GaP buffers grown on GaP nucleation in the Al-free reactor exhibit short misfit dislocations (MDs) and a high density of stacking faults (SFs). In contrast, in the GaP buffers prepared in the Al-containing reactor, the MDs are longer and the density of SFs is lower. Long MDs reduce the lattice strain which results in a smoother GaP surface morphology compared to the GaP buffers with short MDs. GaP buffers grown on modified GaP nucleation layer with Al exhibit even longer MDs, lower density of threading dislocations and very smooth surface morphology. Possibly due to the lower mobility of Al compared to Ga, the surface coverage during the nucleation is improved, which further may affect the crystal quality in the GaP buffer [1].[1] A. C. Lin et al., J. Vac. Sci. Tech. B 29, 3, (2011).

O 61.3 Wed 15:30 H25

Reduction of hydrogen out-effusion by using dense silicon nitride as capping layer — •sahar Jafari — Anhalt University of applied sciences, Köthen, Germany

The dependence of hydrogen effusion out of the a-SiNx:H on its film composition and the form of hydrogen bonds was experimentally studied by using effusion measurement system. Two hydrogen evolution peaks at high and low temperatures were observed but at different temperatures while the sample was heated up to 1000 °C in a constant heat rate (20 °C/min). Regarding the N/Si values revealed from X-ray photo-electron spectroscopy, the increase of N content in SiNx shifts the hydrogen effusion peak to higher temperatures at about 900 °C. It*s assumed that the N-rich silicon nitride can act as a proper capping layer during the contact-firing process (about 800 °C) to reduce the loss of hydrogen. We have confirmed the impact of composition and remained defects at the interface of Si/SiNx and propose an optimized passivation with a stacking structure. Finally, the experimentally observed hydrogen effusion peak has been confirmed by theoretical FEM simulations of Fick*s law.

O 61.4 Wed 15:45 H25

Analysis of the Catalytic Activation of CO_2 by Artificial Intelligence Studies and Extensive DFT Calculations — •Aliaksei Mazheika[1], Yanggang Wang[1,2], Luca Ghiringhelli[1], Sergey V. Levchenko[3,1,4], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, DE — [2]University of Shenzhen, Shenzhen, CN — [3]Skolkovo Innovation Center, Moscow, RU — [4]NUST MISIS, Moscow, RU

Using artificial intelligence (AI) trained on *ab initio* data, we develop a strategy for the rational design of catalytic materials for converting CO_2 to fuels and other useful chemicals. Specifically, we employ the subgroup discovery [1] and sure independence screening and sparsifying operator (SISSO) [2]. For oxide surfaces the results reveal that an electron transfer to the π^* antibonding orbital of the adsorbed molecule and the associated bending of the initially linear O-C-O, previously proposed as indicator of activation [3], are insufficient to account for the good catalytic performance. Instead, our AI model identifies the common feature of a group of experimentally studied oxide catalysts in the binding of one molecular O atom to a surface cation, which results in a strong elongation and therefore weakening of the molecular C-O bond. This suggests to use the C-O bond elongation as an indicator of CO_2 activation. Based on these findings, we propose a set of new promising catalysts for CO_2 conversion, and a recipe to find more.
[1] M. Boley *et al.*, Data Min. Knowl. Disc. **31**, 1391 (2017).
[2] R. Ouyang *et al.*, Phys. Rev. M **2**, 083802 (2018).
[3] H.-J. Freund and M. W. Roberts, Surf. Sci. Rep. **25**, 225 (1996).

O 61.5 Wed 16:00 H25

Mechanisms in Photocatalytic Hydrogen Evolution — •Martin Tschurl, Constantin A. Walenta, Sebastian L. Kollmannsberger, Carla Courtois, and Ueli Heiz — Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

Sustainable energy production and storage is considered one of the major challenges of the future, due to the impact of global warming aggravated by burning fossil fuels. One promising technology to meet this challenge is photocatalysis. It is inspired by the idea to use sunlight for the generation of renewable fuels such as hydrogen. State-of-the-art materials often comprise co-catalyst loaded semiconductors, but these systems are still limited in efficiency. The development of more powerful catalysts may have been hindered by a lack of insights on a molecular scale, as the exact mechanistic details are so far surprisingly little understood. In this talk, detailed mechanisms of the hydrogen evolution on platinum-loaded titania are discussed from a surface science perspective. Different mechanist models to explain hydrogen evolution are discussed and compared with each other.

O 61.6 Wed 16:15 H25

Temperature Influence in the Photocatalysis of Pt-Loaded Titania (110) — •Carla Courtois, Constantin A. Walenta, Sebastian L. Kollmannsberger, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

We show the influence of temperature for the photocatalytic alcohol conversion on an n-type semiconductor single crystal surface. The focus lies on a comparison between different alcohols as reactants on a Pt-loaded titania catalyst. The photooxidation mechanisms proceed via a direct hole transfer to the adsorbed alcohol molecules. The outcome of the photochemical reactions is strongly governed by the thermal adsorption/desorption properties of the involved molecules. Thus, the overall outcome can be controlled by the judicious choice of the reaction conditions.

O 61.7 Wed 16:30 H25

Electronic and Field Induced Manipulation of Diethyl Ether on Si(001) — •Tamam Bohamud[1], Alexa Adamkiewicz[1], Marcel Reutzel[1], Michael Dürr[1,2], and Ulrich Höfer[1] — [1]Philipps-

Universität, 35037 Marburg — [2]Justus-Liebig-Universität Giessen, 35392 Giessen

Scanning tunneling microscopy is an effective tool to manipulate single atoms and molecules on surfaces. Typical excitation processes involved are direct electronic excitation or vibrational excitation via inelastic tunneling. Here we show for diethyl ether fragments on Si(001) that, depending on the tunneling bias, both direct excitation as well as field-induced hopping of the molecular fragments can be observed.

Adsorption of diethyl ether on Si(001) leads to covalently bound ethoxy and ethyl entities on the surface[1]. At room temperature, tip-induced hopping of the ethyl entity on one dimer is observed at relatively low tunneling bias. For this process, no dependence on the tunneling current is observed. On the other hand, for the same parameters but at 50 K surface temperature, no such tip-induced hopping is observed at all. We interpret these experimental results in terms of a field-assisted, thermally activated hopping process. At increased bias voltage, hopping events along the dimer rows were also observed. For this process, a linear dependence of the hopping rate on the tunneling current indicates a direct electronic excitation as origin of the tip-induced hopping process.
[1] M. Reutzel et al., J. Phys. Chem. C. 119, 6018(2015).

O 61.8 Wed 16:45 H25

Quantum Chemical Investigations of Water on Tungsten Trioxide — •Thomas Teusch and Thorsten Klüner — Carl von Ossietzky University Oldenburg, Germany

Tungsten trioxide (WO$_3$) is a promising material for photoanodes, due to its many advantages like the narrower band gap compared to TiO$_2$, which allows for absorption of a large proportion of the solar spectrum. Furthermore, the deep valence band position makes the water oxidation thermodynamically easier and the high electrical conductivity leads to good electron transport properties [1]. We try to understand the involved mechanism in the water oxidation process on an atomistic level. To achieve this, we use quantum mechanical calculations with periodic boundary conditions in terms of hybrid DFT and multiconfigurational methods in terms of complete active space-SCF [2,3]. The latter allows an insight into specific excited states. In this work, we present results of the interaction of WO$_3$(001) with all species occurring in water splitting. In addition, we investigate the oxidation process itself by studying both ground and excited charge transfer states with embedded cluster models. These results provide a molecular view into the water oxidation process and can also be used for high-precision wave-packet quantum dynamics which will allow for new time-resolved insights.

[1] S. Corby, et al., J. Am. Chem. Soc., 2018, 140, 16168-16177 [2] R. Dovesi, et al., Int. J. Quantum Chem. A, 2014, 114, 1287-1317. [3] F. Neese Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2012, 2, 73-78.

O 61.9 Wed 17:00 H25

Proton transfers at dopamine-functionalized TiO2 interface — •Costanza Ronchi[1], Daniele Selli[1], Waranyu Pipornpong[2], and Cristiana Di Valentin[1] — [1]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via R. Cozzi 55, I-20125 Milano, Italy — [2]Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Despite the many successful synthesis and applications of dopamine-functionalized TiO2 nanohybrids,[1],[2], there is not yet an atomistic understanding of the interaction of this 1,2-dihydroxybenzene derivative ligand with the titanium dioxide surfaces. In this work, based on a wide set of dispersion-corrected hybrid density functional theory (DFT) calculations and on density functional tight binding (DFTB) molecular dynamics simulations, we present a detailed study of the adsorption modes, patterns of growth and configurations of dopamine on the anatase (101) TiO2 surface, with reference to the archetype of 1,2-dihydroxybenzene ligands, i.e. cathecol.[3] At low coverage, the isolated dopamine molecule prefers to bend towards the surface, coordinating the NH2 group to a Ti5c ion. Increasing the dopamine coverage, we observed unexpected effects and proton transfers that largely stabilize the self-assembled monolayer.

References

[1] T. Paunesku et al. Nat. Mater. 2003, 2, 343*346.
[2] T. Rajh et al. Nano Lett. 2004, 4, 1017*1023.
[3] L. Liu et al. J. Am. Chem. Soc. 2011, 133, 7816*7823.

O 61.10 Wed 17:15 H25

Reaction Pathways in Heterogeneous Photoreforming of Tertiary Alcohols — •Moritz Eder, Carla Courtois, Kordula Schnabl, Constantin A. Walenta, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

Tertiary alcohols are an ideal model system to investigate mechanisms in photocatalysis. Being organic hydroxyl carriers, they are suitable precursor materials for waste-water purification and biomass conversion. In this talk, we present our most recent results on platinum-loaded titania(110). It is shown that semiconductor photocatalysis selectively enables new reaction pathways, which are not accessible by thermal or conventional chemical methods.