

Surface Science Division

Room D136 - Session SS+2D+AS+HC-WeM

Surface Science of 2D Materials

Moderators: Irene Groot, Leiden University, The Netherlands, Bo-Hong Liu, National Synchrotron Radiation Research Center

8:00am **SS+2D+AS+HC-WeM-1 Heterogeneous Photocatalysis: Alcohols on Bare and Metal-loaded TiO₂(110) and Fe₂O₃(012)**, **Moritz Eder**, TU Wien, Austria; **P. Petzoldt**, **M. Tschurl**, Technical University of Munich, Germany; **J. Pavelec**, **M. Schmid**, **U. Diebold**, TU Wien, Austria; **U. Heiz**, Technical University of Munich, Germany; **G. Parkinson**, TU Wien, Austria

We investigated the (photo)chemistry of alcohols on TiO₂(110) and Fe₂O₃(012) in ultra-high vacuum. Our studies focused on the role of the metal co-catalyst in the photocatalytic reaction by comparing the reactivity of bare and metal-loaded surfaces. We show that photocatalytic reactions are not merely a couple of redox reactions, but an interplay of thermal and photon-driven surface reactions.

Our results demonstrated that the co-catalyst plays a crucial role in the outcome of the reaction. On TiO₂(110), alcohols are oxidized to the aldehyde/ketone and hydrogen surface species upon illumination. The hydrogen surface species were thermally converted to H₂ by the co-catalyst, allowing for a steady-state photocatalytic conversion of alcohols and the continuous production of molecular hydrogen. Using mass spectrometry, we determined turnover frequencies and rate constants. The identification of surface mechanisms on Fe₂O₃ is less advanced, but there seem to be strong parallels in the photochemistry.

Our studies shed light on the fundamental processes involved in photocatalytic reactions on metal-loaded surfaces and contribute to the development of sustainable energy technologies.

8:20am **SS+2D+AS+HC-WeM-2 Factors Governing the Reactivities of Transition Metal Carbides at Vapor/Solid and Liquid/Solid Interfaces**, **S. Alhowity**, **A. Ganesan**, **M. Gharraee**, **O. Omolere**, **Qasim Adesope**, **K. Balogun**, **P. Chukwunenyi**, **F. D'Souza**, **T. Cundari**, **J. Kelber**, University of North Texas

Transition metal carbides are of broad interest for both heterogeneous and electro-catalysis. However, fundamental understanding of chemical factors governing reactivities and selectivities at the vapor/solid and liquid/solid interfaces remain sparse. Herein, *in situ* XPS results, electrochemical measurements, and DFT-based calculations are presented regarding the reactivities of NbC and TaC in the presence of O₂ vapor, and reactivity in solution towards the reduction of N₂ to NH₃. NbC and TaC films were prepared by DC magnetron sputtering deposition, then exposed to O₂ vapor at room temperature, and analyzed by *in situ* XPS without exposure to ambient. Similarly prepared samples were also analyzed by *ex situ* XRD. These data show that, although Nb and Ta have similar oxophilicities, (a) deposited NbC films contain significant amounts of Nb oxide phases throughout the film, whereas TaC films deposited under similar conditions do not, and (b) the exposure of NbC films to O₂ at 300 K results in significant Nb oxide formation, but that TaC films remain inert towards O₂ under these conditions. DFT calculations indicate that this significant reactivity difference towards O₂ is due in large part to the greater Ta-C bond strength compared to Nb-C, and in part due to the relative energetic stabilities of the corresponding oxides. Electrochemical studies show that ambient-exposed NbC, with a Nb₂O₅ surface layer, becomes reactive towards N₂ reduction to NH₃ under acidic conditions, but only after etching in NaOH to remove the surface oxide layer. Additionally, chronoamperometric data indicate that this reactive NbC surface is eventually modified under electrochemical conditions and becomes relatively inert towards N₂ reduction with time. Experiments involving *in situ* sample transfer between UHV and electrochemistry environments demonstrate that electrochemically active NbC surfaces in solution comprise Nb sub-oxide surface layers, in line with previous studies showing that effective NRR catalysts contain surface transition metal ions in intermediate oxidation states, supporting both N₂ lone pair attraction and pi-backbonding to bind and activate the NN triple bond.

Acknowledgement This work was supported in part by the UNT College of Science through COS grants 1600089 and RSG-2023-002 and in part by the NSF under grant no. DMR 2112864.

8:40am **SS+2D+AS+HC-WeM-3 Tunable Interfacial Electrochemistry at Moiré Material Interfaces**, **D. Kwabena Bediako**, University of California at Berkeley

INVITED

At electrode–electrolyte interfaces, crystallographic defects are frequently implicated as active sites that mediate interfacial electron transfer (ET) by introducing high densities of localized electronic states (DOS). However, conventional defects can be challenging to deterministically synthesize and control at an atomic level, challenging the direct study of how electronic localization impacts interfacial reactivity. Azimuthal misalignment of atomically thin layers produces moiré superlattices and alters the electronic band structure, in a manner that is systematically dependent on the interlayer twist angle. Using van der Waals nanofabrication of two-dimensional heterostructures, scanning electrochemical cell microscopy measurements, and four-dimensional scanning transmission electron microscopy, we report a strong twist angle dependence of heterogeneous charge transfer kinetics at twisted bilayer and trilayer graphene electrodes with the greatest enhancement observed near the ‘magic angles’. These effects are driven by the angle-dependent engineering of moiré flat bands that dictate the electron transfer processes with the solution-phase redox couple, and the structure of the relaxed moiré superlattice. Moiré superlattices therefore serve as an unparalleled platform for systematically interrogating and exploiting the dependence of interfacial ET on local electronic structure.

9:20am **SS+2D+AS+HC-WeM-5 Growth of Ultrathin Silica Films on Pt(111) and Rh(111): Influence of Intermixing with the Support**, **Matthias Krinninger**, Technical University of Munich, Germany; **F. Kraushofer**, Technical University of Munich, Austria; **N. Refvik**, University of Alberta, Canada; **F. Esch**, Technical University of Munich, Germany; **B. Lechner**, Technical University of Munich, Austria

Silica is a widely used catalyst support material for clusters and nanoparticles. Understanding the relationship between these clusters and the support is challenging, however, because SiO₂ is insulating, and in most applications not crystalline which drastically limits the use of experimental techniques to those that work on insulating samples and are not diffraction-based. Several previous studies have investigated ultrathin, quasi-2D silica films on a variety of metal supports [1], which can then be measured by scanning tunneling microscopy (STM), XPS and most other surface science methods. Previous work on Pt(111) did not result in closed films, which was attributed to lattice mismatch [2]. We show that closed films can in fact be grown on Pt(111) when silica is deposited in excess, likely due to formation of a platinum silicide layer with slightly expanded lattice constant at the interface. We also report results of film growth on Rh(111), which is a near-perfect match to the lattice constant of freestanding SiO₂ films as calculated by theory. However, no high-quality films were achieved on Rh due to thermodynamic competition with a silicide.

References:

- [1] C. Büchner, M. Heyde, Two-dimensional silica opens new perspectives, *Prog. Surf. Sci.*, 92 (2017) 341-374.
- [2] X. Yu, B. Yang, J. A. Boscoboinik, S. Shaikhutdinov, and H.-J. Freund, *Appl. Phys. Lett.* 100 (2012), 151608.

9:40am **SS+2D+AS+HC-WeM-6 CO₂ Adsorption on Graphitic-Like Bilayer ZnO Film Studied by NAP-XPS**, **Bo-Hong Liu**, **S. Cheng**, National Synchrotron Radiation Research Center, Taiwan

CO₂ activation is a fundamental process in heterogeneous catalysis. ZnO-based catalyst has been extensively used in commercial methanol synthesis from CO₂ gas and the reverse water gas shift reaction. The adsorption behavior of CO₂ on the catalyst surface is pivotal to the reactivity. Whereas ZnO(0001)-Zn physisorbed or weakly chemisorbed CO₂,¹ strong chemisorption of the molecule happens on non-polar surfaces, such as ZnO(10-10), resulting in a tridentate carbonate.² In Operando TEM investigation during methanol synthesis shows that ZnO single atomic layer stacks distortedly around Cu nanoparticles via strong metal-support interaction. The lack of interlayer ordering between the layers suggests a weak interlayer interaction; therefore, each layer resembles a free-standing sheet.³ DFT modeling concluded that free-standing ZnO(0001) layer adopts a graphitic-like co-planer structure. The co-planer feature was verified experimentally for the bi-layer ZnO(0001) supported on Ag(111) and Au(111).⁴ On Au(111) substrate, TPD shows that CO₂ adsorbs on the low coordinate sites at the layer edges.⁵ In the present study, we investigate the CO₂ adsorption on bi-layer ZnO/Ag(111) film using NAP-XPS to extend the

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pressure condition towards reality. We found a more considerable CO₂ chemisorption at elevated pressure. The presentation will also address how the surface hydroxyl group influences CO₂ adsorption.

1. Wang, J.;Hokkanen, B.; Burghaus, U., Adsorption of CO₂ on pristine Zn–ZnO (0 0 0 1) and defected Zn–ZnO (0 0 0 1): A thermal desorption spectroscopy study. *Surf. Sci.* **2005**,577 (2-3), 158-166.
2. Schott, V.;Oberhofer, H.; Birkner, A.;Xu, M.;Wang, Y.;Muhler, M.;Reuter, K.; Wöll, C., Chemical activity of thin oxide layers: strong interactions with the support yield a new thin-film phase of ZnO. *Angewandte Chemie International Edition* **2013**,52 (45), 11925-11929.
3. Lunkenbein, T.;Schumann, J.;Behrens, M.;Schlögl, R.; Willinger, M. G., Formation of a ZnO overlayer in industrial Cu/ZnO/Al₂O₃ catalysts induced by strong metal–support interactions. *Angewandte Chemie* **2015**,127 (15), 4627-4631.
4. Tusche, C.;Meyerheim, H.; Kirschner, J., Observation of depolarized ZnO (0001) monolayers: formation of unreconstructed planar sheets. *Phys. Rev. Lett.* **2007**,99 (2), 026102.
5. Deng, X.;Sorescu, D. C.; Lee, J., Enhanced adsorption of CO₂ at steps of ultrathin ZnO: the importance of Zn–O geometry and coordination. *Phys. Chem. Chem. Phys.* **2017**,19 (7), 5296-5303.

11:00am **SS+2D+AS+HC-WeM-10 Investigation of Nitride Spintronic and Kagome-Structured Intermetallic Topological Materials Using Molecular Beam Epitaxy and Scanning Tunneling Microscopy**, Arthur R. Smith, Ohio University Physics and Astronomy Department

Owing to the overwhelming interest in topological [1] and spintronic materials [2], it is imperative to investigate these down to the atomic scale for their possible use in advanced devices. Many promising properties discovered among nitride materials, such as chemical stability and wide band gaps [3], may be combined with the equally promising aspects of topological materials, such as the topological Hall and Nernst effects [4]. Very recent work illustrates that spin-polarized scanning tunneling microscopy is a powerful tool for exploring topological band-structured Kagome antiferromagnets [5]. In our current work, we investigate both nitride material systems grown using molecular beam epitaxy as well as the growth of topological systems such as Kagome antiferromagnetic materials. Ongoing work in our group encompasses the investigation of Mn₃Sn, FeSn, CrSn, Mn₃Ga, and as a spintronic and topological nitride, Mn₃GaN. These materials are grown in combined UHV MBE and scanning tunneling microscopy chamber systems in which the grown samples are first fabricated using MBE and after that investigated for their structural, electronic, and magnetic properties including using STM and tunneling spectroscopy. Our goal is also to investigate these materials using spin-polarized STM as a function of temperature and applied magnetic field. Our current results show that these materials can be fabricated effectively using molecular beam epitaxy and investigated using various *in-situ* techniques such as reflection high energy electron diffraction and STM. Results from multiple on-going investigations will be presented with a birds-eye view of the progress. Especially to be presented will be STM and STS results in these Kagome systems grown using MBE.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

- [1] P. Liu *et al.*, "Topological nanomaterials," *Nat. Rev. Mater.* **4**, 479 (2019).
- [2] A. Hirohata *et al.*, "Review on spintronics: Principles and device applications," *Journal of Magnetism and Magnetic Materials* **509**, 166711 (2020).
- [3] M. Xu *et al.*, "A review of ultrawide bandgap materials: properties, synthesis and devices," *Oxford Open Materials Science* **2**(1), itac004 (2022).
- [4] S. Roychowdhury *et al.*, "Giant Topological Hall Effect in the Noncollinear Phase of Two-Dimensional Antiferromagnetic Topological Insulator MnBi₄Te₇," *Chemistry of Materials***33**, 8343 (2021).
- [5] H. Li *et al.*, "Spin-polarized imaging of the antiferromagnetic structure and field-tunable bound states in kagome magnet FeSn," *Scientific Reports***12**, 14525 (2022).

11:20am **SS+2D+AS+HC-WeM-11 Molecular Beam Epitaxial Growth and Investigations of FeSn on LaAlO₃**, Tyler Erickson, S. Upadhyay, H. Hall, D. Ingram, S. Kaya, A. Smith, Ohio University

Kagome antiferromagnetic and ferromagnetic materials provide an interesting avenue for research through the investigation of frustrated magnetism, band topology and electronic correlations [1-4]. FeSn is a layer-wise antiferromagnetic Kagome structured material with characteristic dispersion-less flat bands and Dirac cones at the Brillouin zone boundaries. Li *et al.* have presented exciting spin-polarized scanning tunneling microscopy results revealing surface electronic and magnetic properties of *in-situ* cleaved bulk FeSn [1]. Zhang *et al.* reported strain engineering of FeSn on SrTiO₃ (111) with precise control of the stanene layers [2]. Kawakami *et al.* reported Fe₃Sn₂ growth on Pt buffer layers on top of Al₂O₃ and studied various topological phenomena of this topological Kagome material [3,4]. Bhattarai *et al.* studied the magnetotransport properties of FeSn grown on silicon substrates [5]. Here, we study the growth of FeSn directly on LaAlO₃ and report the successful growth of high-quality crystalline thin-films of FeSn. Reflection high-energy electron diffraction and x-ray diffraction are used to discover the *in-plane* and *out-of-plane* lattice constants, while atomic force microscopy and Rutherford backscattering provide topographical and stoichiometric characterization. Preliminary results indicate *in-plane* and *out-of-plane* lattice constants of 5.290 Å and 4.56 Å compared to the expected results of 5.297 Å and 4.481 Å, respectively. Besides discussing the thin film FeSn growth results, we also plan to present scanning tunneling microscopy results on the MBE-grown surfaces.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

- [1] H. Li *et al.*, *Scientific Reports*, 12 14525 (2022)
- [2] H. Zhang *et al.*, *Nano Lett.* **23**, 239 – 2404 (2023)
- [3] I. Lyalin *et al.*, *Nano Lett.* **21**, 6975 – 6982 (2021)
- [4] S. Cheng *et al.*, *APL Mater.* **10**, 061112 (2022)
- [5] N. Bhattarai *et al.*, *Phys. Status Solidi A*, **220**: 2200677 (2023)

11:40am **SS+2D+AS+HC-WeM-12 AVS Graduate Research Awardee Talk: Molecular Beam Epitaxial Growth, Structural Properties, and Surface Studies of α -Plane-Oriented Mn₃Sn on C-Plane Al₂O₃**, Sneha Upadhyay¹, T. Erickson, Ohio University; J. Hernandez, Universidad Autonoma de Puebla, Mexico; H. Hall, K. Sun, Ohio University; G. Cocolletzi, Universidad Autonoma de Puebla, Mexico; N. Takeuchi, Universidad Nacional Autonoma de Mexico, Mexico; A. Smith, Ohio University

Recently, Chen *et al.* reported the observation of tunneling magnetoresistance in an all-antiferromagnetic tunnel junction consisting of Mn₃Sn/MgO/Mn₃Sn.¹ Furthermore, Bangar *et al.* demonstrated a technique for engineering the spin Hall conductivity of Mn₃Sn films by changing the Mn: Sn composition.² These works show the potential of studying this Kagome antiferromagnetic material and the importance of being able to grow smooth films. This work uses molecular beam epitaxy to investigate the growth of Mn₃Sn (11 $\bar{2}$ 0) on Al₂O₃ (0001). The growth is monitored *in-situ* using reflection high energy electron diffraction and measured *ex-situ* using X-ray diffraction, Rutherford backscattering, and atomic force microscopy. In our previous work, we carried out a single-step growth at 450°C, which resulted in a crystalline but discontinuous *α -plane-oriented* (~43% 11 $\bar{2}$ 0) Mn₃Sn film with a mix of other orientations including 0002.³ Leading from this work, changes were made to the growth recipe, which involved carrying out a two-step growth procedure at room temperature, resulting in a contiguous, epitaxial Mn₃Sn film with up to ~82% 11 $\bar{2}$ 0-orientation. We are also exploring the effect of varying the Mn: Sn flux ratio and the film thicknesses (in the range of 5 – 200 nm) on the film crystallinity and orientation. We observe that varying the Mn: Sn flux ratio leads to a change in the RHEED patterns from pointy to streaky, and the XRD shows that the 11 $\bar{2}$ 0 peak can be varied between ~82% to ~38% of all the peaks' total intensity. We also plan to present the first results on ultra-high vacuum scanning tunneling microscopy imaging of the (11- $\bar{2}$ 0) Mn₃Sn surface.

¹ AVS Graduate Research Awardee

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¹ X. Chen *et al.*, "Octupole-driven magnetoresistance in an antiferromagnetic tunnel junction." *Nature* **613**, 490 (2023).

² H. Bangar *et al.*, "Large Spin Hall Conductivity in Epitaxial thin films of Kagome Antiferromagnet Mn₃Sn at room temperature", *Adv. Quantum Technol.* **6**, 2200115 (2023).

³ S. Upadhyay *et al.*, "Molecular beam epitaxy and crystal structure of majority *a*-plane oriented and substrate strained Mn₃Sn thin films grown directly on sapphire (0001)", *Journal of Vacuum Science and Technology A*, to be published (2023).

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