Charles S. Fadley Memorial Session
Room Naupaka Salon 4 - Session CF-MoE2

Charles S. Fadley Memorial Session II: Ambient-Pressure X-ray Photoelectron Spectroscopy

Moderators: Christopher R. Brundle, C.R. Brundle and Associates, **Alexander Gray**, Temple University

7:40pm **CF-MoE2-7 Catching a Wave: From Quantum Materials to Liquid Chemistry***, **Slavomir Nemsak,*** Lawrence Berkeley National Laboratory, USA **INVITED**

Standing-wave photoelectron spectroscopy of multi-layer structures, as pioneered by Prof. Chuck Fadley and his group in the past two decades, proved to be a very powerful technique for probing solid/solid, but also solid/liquid and solid/gas interfaces. Its superior depth selectivity and non-destructive nature were crucial to answer key questions in problems spread over several scientific fields, such as emergent phenomena at complex oxide interfaces [1], artificial multiferroics [2], adsorption mechanisms in liquids [3], corrosion [4], and electrocatalysis [5].These achievements were only possible thanks to innovative approaches both in experiments and analyses, including development of X-ray optical simulations package [6] and its coupling with the black-box optimizer [7]. In this talk I will introduce these tools and highlight their applications to answer diverse scientific problems.

[1] S. Nemsak et al., *Physical Review B***93** (24), 245103 (2016).

[2] H. P. Martins et al., *arXiv preprint arXiv:2012.07993.*

[3] S. Nemsak et al., *Nature Communications***5**, 5441 (2014).

[4] O. Karslioglu et al., *Faraday Discussions***180**, 35 (2015).

[5] C. Baeumer et al., *Nature Materials***20**, 674 (2021).

[6] S.-H. Yang et al., *Journal of Applied Physics***113**, 073513 (2013).

[7] O. Karslioglu et al., *Journal of Electron Spectroscopy and Related Phenomena***230**, 10 (2019).

8:20pm **CF-MoE2-9 High Pressure Hard X-ray XPS Studies of Operando Catalytic Reactions for CO_2 and N_2 Reduction***, **Anders Nilsson,*** Stockholm University, Sweden

Charles Fadley was a pioneer in the field of x-ray photoelectron spectroscopy (XPS) for over 5 decades and I had the pleasure to interact with him frequently since my time at Uppsala University in the 1980s. In the last part of his scientific life he brought forward hard x-ray XPS as an important tool to investigate interfaces. In the following contribution, I would like to honor him with a new direction of hard x-ray XPS that can play an important role for the development of a sustainable society to address climate change and in particular to mitigate CO_2 emissions.

Some of the most essential catalytic reactions for our energy society is to reduce CO_2 to hydrocarbons and alcohols to be used as fuels and base chemicals for the chemical industry. In order to convert a fossil dependent chemical industry and instead use sustainable hydrogen as a feedstock we need to develop new catalysts. Furthermore, the catalytic reduction of N_2 to ammonia has been considered as one of the most important discoveries during the 20th century to produce fertilizers for a growing population. Despite an enormous effort in studying these catalytic reactions we are still lacking experimental information about the chemical state of the catalytic surface and the adsorbates existing as the reaction is turning over.

X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that can provide almost all essential chemical information and it has been developed to operate also in a few mbar of pressure with great success for probing oxidation catalytic reactions. Unfortunately, this pressure regime is too low for the hydrogenation reactions to turn over. However, utilizing the hard x-ray XPS technique can bring the pressure up by many orders of magnitude in an unique instrumentation[1].

Here I will present how Fischer-Tropsch, methanol and ammonia synthesis reactions on single crystal metal surfaces have been probed during operando conditions in the pressure range 100 mbar-1 bar using the new XPS system built at Stockholm University[1] and permanently located at the PETRA III synchrotron in Hamburg. The instrument can vary the incidence angle of the X-rays allowing it to be either surface or bulk sensitive.

[1] P. Amann, D. Degerman, M. T. Lee, J. D. Alexander. M. Shipilin, H. Y. Wang, F. Cavalca, M. Weston, J. Gladh, M. Blom, M. Björkhage, P. Löfgren, C. Schlueter, P. Loemker, K. Ederer, W. Drube, H. Noei, J. Zehetner, H. Wentzel, J. Ålund and A. Nilsson, Rev. Sci. Instrum. **90**, 103102 (2019).

8:40pm **CF-MoE2-10 Initial Oxidation of Ternary Amorphous Metal Alloy Surfaces Under Ambient Oxygen Pressures***, **Gregory Herman,*** Oregon State University*; P. Alzaga,* HP Inc.*; T. Diulus, R. Addou,* Oregon State University*; W. Stickle,* HP Inc.*; J. Jenkins, R. Elzein,* Oregon State University

The oxidation of complex alloys is governed by both thermodynamics and kinetics. The formation of a surface oxide influences a range of surface properties, including catalysis, corrosion resistance, tribology, and others. Further, the structure of ternary alloys can influence oxidation properties, where grain boundaries in polycrystalline samples can provide fast diffusional pathways for oxygen or metal ions/atoms. Amorphous metal thin films (AMTFs) do not have grain boundaries and as a result can have both unique mechanical properties and chemical stability. AMTFs are typically structurally unstable at high temperatures, where they are found to crystallize. Recent studies have developed AMTFs with high thermal stability, including $Ta_{54}W_{27}Si_{19}$. The present research is focused on the characterization of the chemical stability of $Ta_{54}W_{27}Si_{19}$, a ternary AMTF, using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). AP-XPS allows the surface composition and oxidation states of the growing oxide layer to be measured in situ as the AMTFs are heated over a range of temperatures and O_2 partial pressures. Typical experiments were performed at 1 mbar O_2 partial pressure with temperatures ranging from 25 to 300° C. AP-XPS data was obtained with relatively short time intervals and the spectra were modeled using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. This analysis made it possible to determine the rate of oxide growth for the conditions studied, as well as the oxide film composition. Spectral analysis of the AP-XPS data indicated that Ta in $Ta_{54}W_{27}Si_{19}$ films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta_2O_5) layer on the surface. Experiments were also performed on elemental Ta, W, and Si samples, and the results were compared to $Ta_{54}W_{27}Si_{19}$. Analysis of the data indicated that the apparent activation energies for the formation of Ta_2O_5 films on polycrystalline Ta and amorphous $Ta_{54}W_{27}Si_{19}$ films were very similar. However, we found that the oxidation of polycrystalline W and amorphous $Ta_{54}W_{27}Si_{19}$ films were distinctly different. We will discuss these results based on thermodynamic considerations and competitive reactions in the ternary alloys.

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