

Thursday Afternoon, November 9, 2023

Surface Science Division

Room D136 - Session SS+HC-ThA

Alloys and Complex Surfaces

Moderators: Arthur Utz, Tufts University, Zhenrong Zhang, Baylor University

2:20pm **SS+HC-ThA-1 Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico, E Charles Sykes**, Tufts University **INVITED**

In this talk I will discuss a new class of heterogeneous catalysts called *Single-Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency. These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between atomic-scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. In collaboration with Maria Flytzani-Stephanopoulos these concepts derived from our surface science and theoretical calculations have been used to design *Single-Atom Alloy* nanoparticle catalysts that are shown to perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective hydrogenation and dehydrogenation reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis (UCL) and Michaelides (Cambridge University) that predicts reactivity trends for a wide range of *Single-Atom Alloy* combinations for important reaction steps like H-H, C-H, N-H, O-H, and CO₂ activation. Overall, I hope to highlight that this combined surface science, theoretical, and catalyst synthesis and testing approach provides a new and somewhat general method for the a priori design of new heterogeneous catalysts.

3:00pm **SS+HC-ThA-3 Heterogeneities in Early Oxide Evolution on Ni-Cr Alloys Studied with a Combination of XPEEM and Data Analytics Methods, Keithen Orson**, University of Virginia; *W. Blades*, University of Arizona; *Y. Niu*, *A. Zakharov*, Max IV Laboratory, Sweden; *P. Reinke*, University of Virginia

The Ni-Cr alloy system is coveted for its mechanical properties and its resistance to degradation in high-temperature, corrosive environments. This resistance comes primarily from a chemically complex passive film composed of nanometers-thin layer of oxides and hydroxides, but many questions remain about the early stages of passive film growth. Studying this early regime gives insights into how surface orientation and features like grain boundary influence oxide nucleation and growth. The early regime is also where competition between Ni and Cr oxidation occurs on the surface. We studied oxide growth on Ni₂₂wt%Cr using the XPEEM techniques μ -XAS and μ -XPS, giving chemical specificity with a pixel size of 50 nm. We conducted a controlled oxidation on a clean surface with up to 65 L of oxygen at 773 K which records oxide evolution with video rate focused on a region with (212) and (104) surfaces and the corresponding grain boundary. To address the size and complexity of the hyperspectral images we use Principal Component Analysis (PCA) and Non-Negative Matrix Analysis (NNMA) to identify the various spectral components and thus bonding states in the image with spatial and temporal resolution. The Ni L-edge spectra change little over the oxidation process and are characteristic for Ni(0) in line with the known preponderance of Cr oxidation under these conditions. All XAS images include image artifacts mostly seen as modulation of background intensity and slope. Valence band spectra (h ν =95 eV) reveal grain-dependent work function shifts and appear characteristic of the bonding state for O_{ads}. The Cr L-edge shows strong spatial heterogeneities, with NNMA revealing the emergence of chromia nuclei. PCA, while less directly interpretable, gives good qualitative agreement with the NNMA. NNMA analysis informs segmentation of movies taken at a single energy in the Cr-L edge characteristic of oxide. Island nucleation begins between 5 and 20 L of exposure and a logistic growth behavior up to 65L of exposure consistent with Avrami-type nucleation. Chromium oxide particle density and distribution varies widely across the two grains, while particle size remains nearly constant. 21% of the (212) grain is covered evenly by oxide particles, while particle density on (104) is only 11% at the endpoint of the oxidation experiment. A region in the vicinity of the grain boundary on (212) is nearly devoid of chromia particles. In summary, early-stage Ni-Cr oxidation is grain- and texture-

specific with chromia island growth dominating in the 0-65 L oxidation regime. Work function shifts and O adsorbates possibly play a role in these heterogeneities behavior.

3:20pm **SS+HC-ThA-4 The Impact of Crystallographic Orientation on the Oxidation of Ni-Cr Alloys, Petra Reinke**, University of Virginia, USA; *W. Blades*, Arizona State University; *D. Jessup*, *J. St. Martin*, *K. Orson*, University of Virginia, USA

Ni-Cr alloys in the FCC random solid solution structure are coveted for their mechanical properties combined with a superb corrosion resistance and thermal stability. The corrosion resistance in aqueous solution, specifically pitting resistance, can be further improved by addition of a third alloying element such as Mo or W. [1] The role of alloy composition and temperature is well studied but significant knowledge gaps exist in our understanding of the initial oxidation steps until complete oxide layers have formed and Cabrera-Mott type growth models can be applied. The competition between Ni and Cr oxidation plays out at < 873 K of relevance for many energy applications. This regime is highly sensitive to the specifics of surface reactions but also impacted by alloy microstructure. The crystallographic orientation of the surface varies significantly between adjacent grains, and reaches deep into the crystallographic triangle with complex terrace and kink structures. Ni-Cr(100) and Ni-Cr(111) surfaces show highly distinct oxidation pathways modulated by the interfacial epitaxy between NiO and the alloy surface. [2,3] Recent work demonstrated that the pitting resistance in acidic solution is strongly grain orientation dependent. [4] It can be assumed that the orientation of oxide grains in the protective layer leads to contact potentials which influence reactant and vacancy diffusion across the oxide layer as the growth continues.

We will present combined STM, in-situ and operando XPS studies which resolve the oxidation process as a function of crystallographic orientation. We will introduce our approach to identify, and study individual grains with wide variability in surface (h k l) through a combination of metallurgical processing, EBSD, and SEM. The oxidation of individual grains is then be studied and significant variation in oxidation rate and oxide composition are isolated. Thermally induced faceting adds to the complexity of orientation dependent oxidation. It is generally assumed that the epitaxial relation between Ni-Cr and NiO drives its rapid nucleation and layered growth mode. We are extending this assessment beyond the well-studied singular surfaces and calculate structural interfacial models which will also include several chromia surfaces albeit chromia tends to nucleate as sub-oxide surface clusters. [2] The role of interfacial energies in the initial oxidation steps will be assessed for the singular and higher index surfaces.

[1] C. Volders *et al.* npj Materials Degradation **6**, 52 (2022).

[2] W. H. Blades *et al.* ACS Applied Materials & Interfaces **10**, 43219-43229 (2018).

[3] W. H. Blades *et al.* Corrosion Science **209**, 110755 (2022).

[4] K. Gusieva *et al.* The Journal of Physical Chemistry C **122**, 19499-19513 (2018).

3:40pm **SS+HC-ThA-5 Structure of Electrochemical Electrode/Electrolyte Interfaces from First Principles, Axel Groß**, University of Ulm, Germany

Our knowledge about structures and processes at electrochemical electrode-electrolyte interfaces is still rather limited, in spite of its technological relevance in energy conversion and storage. First-principles simulations can help to elucidate these structures in spite of the fact that these simulations are hampered by the complexity of these interfaces together with the fact that the dependence of these interfaces on the electrode potential needs to be properly taken into account. In this contribution, I will first show which insights first-principles calculations can provide with respect to halide and sulfate adsorbate structures at electrochemical interfaces [1,2] using grand-conical approaches yielding reliable Pourbaix diagrams of the stable adsorbate phases. Furthermore I will demonstrate how ab initio molecular dynamics simulations can contribute to a better understanding of the structure of electric double layers at metal electrodes [3,4]. The presentation will conclude with some general remarks about remaining challenges in our understanding of electrochemical electrolyte/electrode interfaces [5].

References

- [1] F. Gossenberger, F. Juarez, and A. Groß, *Front. Chem.* **8**, 634 (2020).
- [2] A. Groß, *J. Phys. Chem. C* **126**, 11439 (2022).
- [3] S. Sakong and Axel Groß, *Phys. Chem. Chem. Phys.* **22**, 10431 (2020).

[4] A. Groß and S. Sakong, Chem. Rev. 122 , 10746–10776 (2022).

[5] A. Groß, Curr. Opin. Electrochem. 40, 101345 (2023).

4:00pm **SS+HC-ThA-6 Surface Characteristics of Flexible Carbon-Doped Oxide Thin Films Under Reactive Ion Etching Process Using Fluorocarbon-Based Plasma**, *Seonhee Jang, T. Poche, R. Chowdhury*, University of Louisiana at Lafayette

The microelectronics industry is increasing research on flexible electronics. Instead of the traditional rigid Si-based electronics, flexible electronics utilize polymer substrates that allow stretching, bending, and folding of the device, which drastically expand its applications. A wide variety of inorganic materials, semiconductors, dielectrics, and metals have been integrated for the fabrication of flexible electronic devices. One of the dielectric materials employed in semiconductor devices is carbon-doped silicon oxide (SiCOH). In this study, flexible low-k SiCOH films were produced by plasma-enhanced chemical vapor deposition (PECVD) of tetrakis(trimethylsilyloxy)silane ($C_{12}H_{36}O_4Si_5$) precursor onto flexible indium tin oxide/polyethylene naphthalate (ITO/PEN) substrates using a set of different plasma powers, yielding the films with varying material properties. The physical properties including refractive index, extinction coefficient, surface morphology and roughness, and surface wettability were determined. The surface structures were analyzed by Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectra. Four prominent peaks of Si-O-Si stretching, Si-CH₃ bending, Si-(CH₃)_x stretching, and CH_x stretching modes were observed in the FTIR spectra. High-resolution XPS spectra of Si2p, C1s, and F1s were analyzed for the chemical bond structure and elemental composition. Mechanical properties including elastic modulus and hardness were measured using nanoindentation. The pristine SiCOH films were then subjected to an inductively coupled plasma-reactive ion etching (ICP-RIE) process. The etching properties of the flexible SiCOH films were characterized under a set of fluorocarbon (CF₄)-based plasmas such as CF₄, CF₄+O₂, and CF₄+Ar. The CF₄ flow rate was maintained at 35 sccm while the O₂ and Ar flow rates were both at 24 sccm. The RF plasma at 13.56 MHz was maintained at 200 W and the ICP power at 40 W. The operating pressure and temperature were 10.0 Pa and ambient temperature, respectively. The duration for etching process was 30 s. Using deconvolution of FTIR and XPS spectra, the surface structures of the SiCOH films after etching process were compared with those of the pristine film. The fraction ratios of the deconvoluted peaks in each prominent peak in the FTIR spectra depended on the deposition plasma power and RIE etching gas composition. In the XPS spectra analysis, each Si2p and C1s peak showed a depressed peak intensity after etching process. With additional etchants of O₂ and Ar, the F1s peak shifted to higher binding energy for lower deposition plasma power and lower binding energy for higher deposition plasma power. Surface properties of flexible SiCOH films after etching were changed according to composition of etchants.

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