Surface Science Division
Room D136 - Session SS+AS+TF-MoA

Mechanisms at Surfaces and Interfaces

Moderators: Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, **Jun Nakamura**, UEC Tokyo

1:40pm **SS+AS+TF-MoA-1 Spin- and Alignment-Controlled O_2 Chemisorption and Catalytic CO Oxidation on Stepped Pt and Pt/Co Alloy Surfaces***, Mitsunori Kurahashi,* National Institutes for Materials Science, Japan **INVITED**

O_2 chemisorption and catalytic oxidation on Pt and its alloy surfaces have been studied intensively due to the relevance to important processes such as car exhaust gas purification and oxygen reduction reaction (ORR) in fuel cell. Since O_2 is a linear diatomic molecule with an electron spin, the alignment of the O_2 axis relative to the surface local structure is a key to understand the elementary processes of O_2 chemisorption. If the surface is magnetic, the spin correlation between O_2 and the surface also plays an important role. A single spin-rotational state-selected [(J,M)=(2,2)] O_2 beam allows us to investigate the effects of molecular alignment and spin on O_2/surface interactions [1].

In this talk, I will firstly present the alignment-controlled O_2 chemisorption and CO oxidation on curved Pt(111). The use of a curved crystal surface and a local probe allows us to monitor the step-density dependence in surface properties or reactivity[2,3]. In this study, by scanning the aligned O_2 beam with a dimension of 0.2mmW x 2mm across a curved Pt(111) surface, the step-density and structure dependence in alignment-resolved O_2 chemisorption probability and CO oxidation rate were measured. The results indicate that step affects the reactivity of the neighboring terraces, and that the low temperature CO oxidation rate at step site is much lower than at (111) terrace.

Secondly, I will present the spin-dependent catalytic CO oxidation on Pt/Co/Pt(111). Pt/Co alloy has attracted much attention since it shows a higher ORR activity than pure Pt [4]. The higher reactivity has been attributed to the charge transfer from the subsurface Co to the surface Pt layer while how the spin of the subsurface Co affects the reactivity of the surface Pt remains unclear. Spin-resolved O_2 chemisorption and CO oxidation experiments on a perpendicularly-magnetized Pt/Co(2ML)/Pt(111) film indicate that the O_2 chemisorption probability and the catalytic oxidation rate depend strongly on the spin orientation between O_2 and the Pt surface. The magnitude of the spin orientation dependence was larger than that observed for O_2/Ni [1,5]. An SPMDS measurement and DFT calculation show that the surface Pt layer is spin-polarized at around E_F. The present experiments indicate that the catalytic activity of Pt is strongly affected by the magnetism of neighboring atoms.

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2:20pm **SS+AS+TF-MoA-3 Atomic-Scale Insights Into the Sintering Resistance and Oxidation of Single-Atom Alloys***, Audrey Dannar*[1]*,* Tufts University*; J. Finzel,* University of California, Santa Barbara*; V. Cinar, E. Sykes,* Tufts University

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes that can take place in oxidizing environments, where Cu is known to readily oxidize to form CuOx, and reducing environments, where Cu is known to deactivate via sintering. Single-atom alloys (SAAs) are a new type of catalyst in which isolated atoms of dilute reactive dopants such as Pt and Rh are present in more inert host metals such as Cu. Despite their great promise for hydrogenation and dehydrogenation reactions, there exists limited understanding of these materials under oxidizing conditions. Similarly, SAAs have shown exceptional long-term stability with anecdotal reports of sintering resistance in industrial conditions that are not presently fundamentally understood. This work aims to develop atomic-scale structure-function relationships for Cu-based catalysts that span oxidizing and reducing conditions and understand how single dopant atoms stabilize the undercoordinated Cu atoms responsible for sintering and involved in CuOx formation upon O2 exposure.

First, we used a specialized method for measuring the surface diffusion of metal atoms that leads to sintering with scanning tunneling microscopy (STM) experiments which reveals that single Pt atoms in a Cu(110) surface significantly reduce the rate of Cu atom detachment from undercoordinated surface sites. Thus, the origin of sintering resistance exhibited by SAA is hypothesized to be due to dopant atom stabilization of undercoordinated Cu atoms at the step edge. This is validated by DFT and paired with collaborator work that shows PtCu/SiO2 dilute alloy catalysts are significantly more stable than monometallic Cu/SiO2 in methanol synthesis experiments via EXAFS and TEM.

Next we used STM experiments to elucidate atomic-scale details of the oxidation processes of both PtCu(111) and RhCu(111) SAAs. STM images reveal that on Cu(111), oxidation occurs below Cu step edges, consistent with literature reports. Interestingly, for the RhCu(111) SAA, oxidation occurs both below the step edges and also above, where the Rh atoms are located, but this is not the case for the Pt brim on PtCu(111). For both Rh and Pt SAAs the oxidation below the step edge is reduced compared to Cu, which we hypothesize is due to the stabilization of Cu step edge atoms, which are required to restructure during CuOx formation below the step. The reduced rates of sintering and oxidation of PtCu SAAs compared to Cu originate from Cu step edge atoms being kinetically stabilized by dilute dopants. Together, these results begin to shed light on the role of single dopant atoms in the mechanisms Cu nanoparticle sintering and Cu oxidation.

2:40pm **SS+AS+TF-MoA-4 Visualization of the Local Dipole Moment at the Si(111)-(2x2) Surface Using DFT Calculations***, Akira Sumiyoshi, J. Nakamura,* The University of Electro-Communications (UEC Tokyo), Japan

Understanding the polarization state of a sample is essential in the development of devices and functional materials. Recently, the spatial distribution of the surface polarization has been observed using new microscopy techniques, such as SNDM[1-3]. However, there have yet to be any reports regarding the theoretical simulation of surface polarization. Here, we focused on the dipole moment (DM), an essential aspect of polarization, and developed a method to visualize the distribution of surface DM using theoretical calculations. In this study, we report on the surface DM distribution of Si(111)-(2x2) with the characteristic motif of the Si(111)-(7x7) DAS structure. Furthermore, we confirmed that the surface dipole distribution can be explained consistently with the surface stabilization mechanism.

We defined and calculated the DM using the following formula;

$\mu_{(x,y,z)} = \int \rho_{(x,y,z')} * (z'-z_0)\, dz'$

Here, μ is the DM, $\rho_{(x,y,z')}$ is the total charge density, and z_0 is the origin in the vertical direction. In order to eliminate the effect of the backside surface of the Si(111) slab, we adopted the midpoint of the deepest bulk layer of the slab as the origin and integrated the above formula from z_0 to the vacuum position z sufficiently far from the topmost surface. The total charge density was calculated using DFT-based first-principles calculations.

Upon optimizing the structure, the restatom was lifted compared to the original bulk position, suggesting the larger orbital electronegativity[4] of the surface orbital of the restatom[5]. This change in orbital electronegativity leads to an electron transfer from the adatom to the restatom, resulting in no surface dangling bond. We calculated the electron localization function (ELF) map and the band diagram to confirm the surface electron transfer. We confirmed the presence of the electron pair on the restatom from ELF. It was revealed that the Si(111)-(2x2) surface has a finite energy gap. As a result, it was clearly shown that the electron transfer occurs from the adatom to the restatom, emptying the dangling bond at the adatom and forming a lone pair at the restatom.

Furthermore, we simulated the surface DM distribution. As a result, an upward DM was observed at the adatom position, which is explained by the depletion of electrons just above the adatom due to the electron transfer at the surface.

[1] Yasuo Cho et al., Phys. Rev. Lett. 99, 186101(2007)

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[4] Jun Nakamura et al., J. Phys. Soc. Jpn. 66, 1656(1997)

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[1] **SSD Morton S. Traum Award Finalist**

3:00pm **SS+AS+TF-MoA-5 Mechanism Study of a Chemisorbed O_2 Molecule on Ag(110) Induced by High-Order Overtone Excitation Using STM***, **Minhui Lee**, E. Kazuma,* The University of Tokyo, Japan*; C. Zhang,* Tongji University, China*; M. Trenary,* University of Illinois at Chicago*; J. Takeya,* The University of Tokyo, Japan*; J. Jung,* University of Ulsan, Republic of Korea*; Y. Kim,* The University of Tokyo, Japan

The dissociation pathway of chemisorbed O_2 on Ag(110) was elucidated by single-molecule microscopic and spectroscopic studies using a scanning tunneling microscope (STM). The dissociation reaction was found to be predominantly triggered by inelastically tunneled holes from the STM tip due to the significantly distributed density of states below the Fermi level of the substrate. A combination of action spectroscopy with the STM and density functional theory calculations revealed that the O_2 dissociation reaction is caused by direct ladder-climbing excitation of the high-order overtones of the O-O stretching mode arising from anharmonicity enhanced by molecule-surface interactions.

3:20pm **SS+AS+TF-MoA-6 Characterization of Oxygen Evolution from Rh(111)***, **Maxwell Gillum**, E. Jamka, F. Lewis, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed reactions, it is critical to gain a fundamental understanding of the reactivity and behavior of oxygen on these transition metal surfaces. In previous studies we have been able to establish that the reactivity and thermodynamic stability of oxygen on Rh(111) relies in part on the concentration of oxygen present in the subsurface. However, more research needs to be conducted in order to gain a better understanding of the relationship between surface reactivity and subsurface concentration. In addition to the techniques used in our previous studies, namely temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), the experiments herein will include simultaneous infrared (IR)/TPD techniques to gain more information on these critical interactions.

4:00pm **SS+AS+TF-MoA-8 Spin-Polarized VLEED from Au(111): Surface Sensitivity of the Scattering Process***, **Christoph Angrick**, A. Reimann,* University of Münster, Germany*; J. Braun,* Ludwig-Maximilians-University of Munich, Germany*; M. Donath,* University of Münster, Germany

Low-energy electron diffraction from Au(111) shows the well-known threefold symmetry of the diffracted electron beams despite the sixfold symmetry of the surface layer. This is due to the influence of the second and deeper layers and the probing depth of the electrons. In this work, we investigated Au(111) with spin-polarized very-low-energy electron diffraction (VLEED) [1,2,3] experimentally and theoretically. We monitor the reflected specular beam at a fixed polar angle of incidence of Θ=45° while the azimuthal orientation of the crystal is varied. This puts the surface sensitivity of the VLEED scattering process to a test.

Our results show that the electron reflection and the spin-orbit-induced reflection asymmetry along ΓM and ΓM' are equivalent. The observed sixfold symmetry suggests a sensitivity to one atomic layer only. At azimuth angles deviating from the high-symmetry directions ΓM and ΓM', however, the VLEED signal from Au(111) shows a threefold symmetry. To reveal the origin of this effect, we varied the parameters in the calculation. The results indicate a non-negligible influence of the second atomic layer in the VLEED scattering process.

[1] Burgbacher *et al.*, Phys. Rev. B **87**, 195411 (2013).

[2] Thiede *et al.*, Phys. Rev. Applied **1**, 054003 (2014).

[3] Angrick *et al.*, J. Phys.: Condens. Matter **33**, 115001 (2020).

4:20pm **SS+AS+TF-MoA-9 Unravelling the Chemisorption Mechanism of Epoxy-Amine Coatings on Zr-Based Converted Galvanized Steel by Combined Static XPS/ToF-SIMS Approach***, **Vanina Cristaudo**, K. Baert, P. Laha,* Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel, Belgium*; M. Lim, L. Steely, D. Clingerman, E. Brown-Tseng,* Coatings Innovation Center, PPG*; H. Terryn, T. Hauffman,* Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel, Belgium

In the automotive industry, the corrosion protection of hot-dip galvanized (HDG) steel is of primary importance. To this purpose, a Zr oxide-based conversion pre-treatment of the metal surface for passivation and improved adhesion [1], in combination with the application of a polymeric primer coating is often performed. Usually, organic and inorganic additives are used in the acidic conversion bath for a large variety of purposes. For instance, Cu(II) salts are employed to accelerate the deposition of zirconium oxide [1]. Recently, the heterogeneity and multi-metal nature of the resulting surface has been demonstrated in our laboratory [2]. Now, it is of pivotal importance to study the efficiency and durability of such hybrid (hydr)oxide-polymer systems, which depend on the formation and degradation of the chemical bonds at the buried interface.

This work aims at the elucidation of the interfacial interactions established between an epoxy-amine coating and HDG steel [3]. The influences of the Zr-based conversion treatment of the substrate and the use of Cu(II) additive on interfacial bonding will be studied [3]. To this purpose, an amine-functionalized molecule – diethylenetriamine (DETA), a common curing agent – will be adsorbed and used as an indicator of the acid-base properties of the metal oxide surface. The complex multi-metal oxide surface of the Cu-modified Zr-based converted substrate will be decomposed in derivative (simpler) systems, such as pure Zn, Zr, and Cu. The resulting DETA-adsorbed model and multi-metal surfaces will be investigated by X-ray photo-electron spectroscopy (XPS), and by examination of the N 1s peak, the interfacial bond densities will be determined. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) will be performed to discriminate between the different metal oxide contributions present on the substrate surface. Preferential adsorption of the DETA molecule on the zinc atoms is found on converted substrates. SIMS also points out the interfacial bonding with the Cu cationic sites when the copper additive is used, highlighting the extreme usefulness of this analytical technique in the assessment of interfacial interactions of "diluted" adsorption sites.

References

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[3]V. Cristaudo, *et al.* Unravelling the chemisorption mechanism of epoxy-amine coatings on Zr-based converted galvanized steel by combined static XPS/ToF-SIMS approach. Appl. Surf. Sci. (2022), 599, p.153798.

4:40pm **SS+AS+TF-MoA-10 Fermi Surface Emergence and Valence Band Maximum Formation During Li_xCoO_2 Insulator-to-Metal Transition***, **Elena Salagre**,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid, Spain*; P. Segovia,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid. IFIMAC (Condensed Matter Physics Center), Spain*; M. González-Barrio,* Dpto Física de Materiales, Universidad Complutense de Madrid, Spain*; J. Pearson, I. Takeuchi,* Materials Science and Engineering, Univ. Of Maryland*; E. Fuller, A. Talin,* Sandia National Laboratories*; M. Jugovac, P. Moras,* Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Italy*; A. Mascaraque,* Dto. Fïsica de Materiales, Univ. Complutense de Madrid, Spain*; E. Garcia Michel,* Dto. Física Materia Condensada, Univ. Autonoma de Madrid, IFIMAC (Condensed Matter Physics Center), Spain

Despite the great interest in $LiCoO_2$ (LCO) and related materials for their applications in batteries, catalysis and resistive memory devices, uncertainties regarding the valence band structure, charge compensation and the nature of the insulator-to-metal transition (IMT) remain controversial [1][2]. In addition, the use of chemical and electrochemical methods on heterogeneous materials, including cathode binders and solid electrolyte interfaces, pushes research further away from a fundamental understanding of the processes involved in ion deintercalation.

We have developed a surface science-based approach to vary the Li content, based on Ne^+ sputtering and performed entirely in situ under ultra-high vacuum (UHV) conditions on epitaxial LCO thin films, without interactions between the material and any electrolyte.

This has allowed us to obtain high-resolution angle-resolved photoemission (ARPES) data of the valence band structure in LCO for a wide range of Li molar fractions, directly observing the IMT at x=0.95 and the regions of phase coexistence and phase dominance. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used to characterize the material during Li deintercalation and to investigate the mechanisms of charge compensation in the absence of electrolyte. Li removal is accompanied by the formation of Co^{4+} from the initial Co^{3+} in the LCO structure. Oxygen holes were also observed, related to the hybridization of Co 3d and O 2p orbitals. The valence band was interpreted using reported theoretical calculations [3] and limited previous experimental work [4]. We identify the Co 3d t_{2g} energy levels as those involved in the IMT and locate the valence band maxima (VBM) with a clear 3-fold symmetry and band renormalization, suggesting a Mott character of the transition.

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[4] *Y. Okamoto et al., «Electronic structure and polar catastrophe at the surface of Lix CoO2 studied by angle-resolved photoemission spectroscopy», Phys. Rev. B, vol. 96, n.º 12, p. 125147, 2017*

5:00pm **SS+AS+TF-MoA-11 Nanoscale Hydrogen Detection Using Time-of-Flight Secondary Ion Mass Spectrometry***, B. Paudel, J. Dhas, M. Choi, Y. Du,* ***Zihua Zhu,*** Pacific Northwest National Laboratory

Hydrogen in materials attracts tremendous interest as its incorporation leads to significant alterations in structure, composition, and chemistry, which in turn impacts functional properties. Additionally, it has been integral to nuclear fusion reactors and is regarded as the major source of clean energy. However, nanoscale manipulation and characterization of hydrogen in materials are challenging as only a selected few analytical technique can readily detect hydrogen, among which time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a unique and powerful technique due to its excellent detection limit along with decent spatial and depth resolutions. In our lab, ToF-SIMS has been used for hydrogen detection for more than 15 years, and it became more and more important in the last several years. In this presentation, we will discuss, using selected examples, how the detection and quantification of hydrogen in materials by ToF-SIMS has been utilized to reveal the hydrogenation/protonation-induced novel functional states in different classes of materials along with some tricks on sample preparation, optimized experimental conditions to achieve reasonable detection limits of hydrogen, and future prospects. We emphasize the unique capabilities of ToF-SIMS which can potentially unlock new functional states and answer some outstanding scientific questions in materials science.

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