Applied Surface Science Division
Room 204 - Session AS-TuA

The Impact of Modeling (Ion, Electron) and Data Analysis on Applied Surface Science, a Celebration of the Career of Barbara Garrison

Moderators: Gregory L. Fisher, Physical Electronics, Alexander Shard, National Physical Laboratory

2:20pm **AS-TuA-1 Collective Action, the Key to Soft Molecule Desorption under Particle Bombardment**, ***Arnaud Delcorte,*** Université catholique de Louvain, Belgium **INVITED**

The focus of this contribution is on desorption of large non-volatile organic molecules induced by ion beams, for 2D and 3D analysis by secondary ion mass spectrometry (SIMS). It is also the story of my long-term collaboration with Pr. Barbara Garrison since 1999, when I started my post-doc under her guidance. Our first molecular dynamics (MD) simulations of polystyrene emission from silver induced by atomic projectiles gave us direction: in order to emit large molecules with minimal internal energy, collective action of the substrate atoms was required, which only occurred in so-called high (sputter) yield events where most of the projectile energy was deposited in the extreme surface [1]. These high yield events, rare with atomic ions, happened to be the rule with cluster projectiles such as C_{60}, where the collision cascades fully overlapped [2]. The use of C_{60} therefore led to remarkable sputtering yield enhancements for organic samples, and much improved emission of molecular ions in SIMS [3]. Clusters were the solution. We then naturally moved to larger clusters, where the physics shifted again, to macroscopic-like impacts phenomena [4]. Our simulations using large organic and argon clusters showed similar trends and, in particular, they quantitatively predicted the experimental 'universal' sputtering curves for the Ar cluster bombardment of organics [5]. The simulations also uncovered a region of energy, scaled by the number of atoms in the projectile (E/n), where fragmentation was minimized and intact molecular emission, maximized. All of this could not have been achieved without the great collective spirit and action that were maintained by Pr. Garrison in her 'extended team' over the years.

[1] A. Delcorte and B. J. Garrison, *High Yield Events of Molecular Emission Induced by Kiloelectronvolt Particle Bombardment*, J. Phys. Chem. B2000, *104,* 6785.

[2] A. Delcorte and B. J. Garrison, *Sputtering Polymers with Buckminsterfullerene Projectiles: A Coarse-Grain Molecular Dynamics Study*, J. Phys. Chem. C2007, *111,* 15312.

[3] D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill, J. C. Vickerman, *A C60 Primary Ion Beam System for Time of Flight Secondary Ion Mass Spectrometry: Its Development and Secondary Ion Yield Characteristics*, Anal. Chem. 2003, 75, 1754.

[4] A. Delcorte, B. J. Garrison, K. Hamraoui, *Dynamics of Molecular Impacts on Soft Materials: From Fullerenes to Organic Nanodrops*, Anal. Chem.2009, *81,* 6676.

[5] A. Delcorte and M. Debongnie, *Macromolecular Sample Sputtering by Large Ar and CH4 Clusters: Elucidating Chain Size and Projectile Effects with Molecular Dynamics,* J. Phys. Chem. C 2015, 119, 25868.

3:00pm **AS-TuA-3 Mechanisms of the Generation of Nanoparticles and Surface Modification in Short Pulse Laser Ablation of Metal Targets in Liquids**, ***Leonid Zhigilei,*** *C Shih, M Shugaev,* University of Virginia

The ability of short pulse laser ablation in liquids to produce clean colloidal nanoparticles and unusual surface morphology has been employed in a broad range of practical applications. In this presentation, the results of large-scale molecular dynamics simulations aimed at revealing the key processes that control the surface morphology and nanoparticle size distributions generated by pulsed laser ablation in liquids [1-4]. The simulations of Ag and Cr targets irradiated in water are performed with an advanced computational model combining a coarse-grained representation of liquid environment and an atomistic description of laser interaction with metal targets. One of the interesting predictions of simulations performed at sufficiently high laser fluences, in the regime of phase explosion, is the emergence of Rayleigh–Taylor and Richtmyer–Meshkov hydrodynamic instabilities at the interface between ablation plume and superheated water, leading to the formation of nanojets and emission of large droplets into the water environment. The droplets are rapidly quenched and solidified into nanoparticles featuring complex microstructure and metastable phases, as demonstrated by example structures shown in the middle of the cover. Rapid nucleation and growth of small nanoparticles in the silver–water mixing region and the breakup of the hot metal layer into larger droplets due to the hydrodynamic instabilities represent two distinct mechanisms of the nanoparticle formation that yield nanoparticles of two different size ranges as early as several nanoseconds after the laser irradiation. This computational prediction provides a plausible explanation for experimental observations of bimodal nanoparticle size distributions in short pulse laser ablation experiments.

[1] **C.-Y. Shih *et al.*, J. Colloid Interface Sci. 489, 3-17, 2017**.

[2] M. V. Shugaev *et al.*, Appl. Surf. Sci. **417**, 54-63, 2017.

[3] C.-Y. Shih *et al.*, J. Phys. Chem. C **121**, 16549-16567, 2017.

[4] C.-Y. Shih *et al*., Nanoscale **10**, 6900-6910, 2018.

3:20pm **AS-TuA-4 First Principles Thermodynamics and Molecular Modeling of Surfaces in Aqueous Environments**, ***Donald Brenner,*** *Z Rak, L Su, J Krim,* North Carolina State University

We have been using first-principles thermodynamics and molecular modeling to characterize the structure, stability and dynamics of solid surfaces in aqueous environments. This talk will focus on two recent examples from our research. The first involves understanding and predicting the thermodynamics of the corrosion of stainless steel and nickel alloys in contact with the coolant in nuclear pressurized water reactors, as well as the driving force that leads to unwanted deposits on the fuel rod cladding from the corrosion products. The second example is a molecular modeling study of the adhesion of functionalized nano-diamond clusters to a gold substrate. Our simulations have revealed a new phenomenon, a molecular water layer containing solvated counter ions between a gold substrate and a negative nano-diamond that is facilitated by surface functionalization, and that is not present for a positively charged nano-diamond. The resulting electro-static screening leads to a weaker adhesion of negative nano-diamonds compared to positive nano-diamonds, an effect that has been observed in prior experiments but not understood.

This work was supported by the Consortium for Advanced Simulation of Light-Water Reactors, a DoE Energy Hub, and by the National Science Foundation through grant DMR-1535082.

4:20pm **AS-TuA-7 Computer Modeling of Cluster Projectile Impacts for SIMS Applications**, ***Zbigniew Postawa,*** Jagiellonian University, Krakow, Poland **INVITED**

A few years ago, Secondary Ion Mass Spectrometry (SIMS) has celebrated its centennial. The first observation of secondary ions is credited to J.J. Thompson at the beginning of the twentieth century [1]. However, the golden era of SIMS began in the fifties and continues to this day. This period is associated with a plethora of ground-breaking equipment developments, experimental observations and theoretical explanations. Initially, theoretical descriptions were based on analytical models. However, soon it has been realized that a proper description of phenomena taking place in more complex materials goes beyond the capability of this treatment. The appearance of computers and computer simulations have breathed new life into the field [2]. Today, computer simulations are a vital counterpart to the experimental measurements due to the atomic resolution and ability to visualize processes taking place inside investigated solids. As ion beams have developed from argon, through gallium, gold, bismuth to metal clusters, C_{60} and now giant atomic and molecular clusters and as computers have become ever more powerful, analysis and simulation of ever more realistic materials has gone forward hand in hand. Barbara Garrison has been always at the forefront of all these endeavors.

In this talk, a few examples of theoretical studies, which Barbara has guided and/or inspired, will be given. Examples include efforts to understand a difference in processes stimulated by impacts of atomic and cluster projectiles [3], evolution of surface roughness during cluster bombardment and its influence on the depth resolution in depth profiling [4], and processes of molecular emission from cluster-bombarded novel ultra-thin graphene-based substrates used recently to enhance molecular ionization [5].

[1] J.J. Thompson, Rays of Positive Electricity, Philos. Mag. 20 (1910) 752.

[2] B.J. Garrison and Z. Postawa, *Molecular Dynamics Simulations, the Theoretical Partner to dynamic cluster SIMS Experiments*, in *ToF-SIMS - Surface Analysis by Mass Spectrometry - 2nd Edition*, Eds. D. Briggs and J.

Vickerman (SurfaceSpectra Ltd/IM Publications, 2013) *and reference therein*.

[3] Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, *Microscopic Insights into the Sputtering of Ag{111} Induced by C_{60} and Ga Bombardment of Ag{111}*, J. Phys. Chem. B 108 (2004) 7831.

[4] D. Maciazek, R. Paruch, Z. Postawa, B.J Garrison, Micro- and Macroscopic Modeling of Sputter Depth Profiling, J. Phys. Chem. C 120 (2016) 25473.

[5] S. Verkhoturov, M. Gołuński, D. Verkhoturov, S. Geng, Z. Postawa, and E. Schweikert, Trampoline, J. Chem. Phys. **148** (2018) 144309.

5:00pm **AS-TuA-9 Use of Ion-Solid Interactions Modeling and Theory for Real Applications in FIB Milling***, **Lucille Giannuzzi***, L.A. Giannuzzi & Associates LLC

Many FIB techniques in sample preparation and prototyping have been developed with a knowledge and use of ion-solid interactions modeling and theory. Understanding ion-solid interactions at different incident angle, ion energy, dose, and effect of target crystallography, are crucial for quality FIB milling of materials [1,2]. A discussion on the modeling and theory of ion-solid interactions and its direct influence on FIB milling quality and results will be presented.

[1]Lucille A. Giannuzzi, Remco Geurts, and Jan Ringnalda,Microsc Microanal 11(Suppl 2), 828-829, 2005

[2]Michael F. Russo, Jr., Mostafa Maazouz, Lucille A. Giannuzzi, Clive Chandler, Mark Utlaut, and Barbara J. Garrison, Microsc. Microanal. 14, 315–320, 2008

5:20pm **AS-TuA-10 The Influence of the Projectile Cluster on the Molecular Ionization Probability in SIMS***, **Lars Breuer**, A Wucher,* Universität Duisburg-Essen, Germany*; N Winograd,* The Pennsylvania State University

The implementation of cluster ion sources in secondary ion mass spectrometry (SIMS) opened the field to molecular imaging and depth profiling of organic materials. In the last years the trend to larger projectiles continued and led to gas cluster ion beams (GCIB) with projectiles consisting of thousands of atoms. The use of these projectiles not only reduces the chemical damage produced by the projectile impact and therefor preserves the molecular information, but also significantly increases the sputter yield of organic material. For the measured signal in a ToF-SIMS experiment the secondary ion yield is of greater interest. Here describes the probability that an intact quasi-molecular ion of species *i* is formed during the sputtering process. As for inorganics especially metals a long list of values for ionization probabilities has been reported in the literature only very little is known about ionization probabilities of organic molecules in particular under GCIB bombardment.

The knowledge of ionization probabilities and sputter yields is of great general importance. Not only is the process of ion formation not fully understood yet, but also can manipulating the ionization probability increase the sensitivity of the experiment. Possible approaches for such manipulations are changes is projectile size, kinetic energy and chemistry. The important question here is: “How much headroom is left to produce more secondary ions?”

To answer this question a measurement of the ion fraction in the flux of sputtered material is necessary. Such a measurement requires the direct comparison of the sputtered intact secondary (quasi-) molecular ion and its neutral counterparts. To perform such a measurement post-ionization without severe photo-fragmentation has to be performed. In our measurements we used a strong-field post-ionization scheme due to its universality and low fragmentation. In the past our lab performed this kind of measurements on material sputtered under C_{60} bombardment [1,2] which has been extended to the bombardment with GCIB in this study. As a result, we will compare ionization probabilities of sputtered molecular species under GCIB and C_{60} bombardment.

[1] Popczun, N.J., Breuer, L., Wucher, A. and Winograd, N., J. Am. Soc. Mass Spectrom. (2017) 28: 1182.

[2] Popczun, N.J., Breuer, L., Wucher, A. and Winograd, N., J. Phys. Chem. C 2017 121 (16), 8931-8937.

5:40pm **AS-TuA-11 In Situ Liquid SIMS, a Molecular Eye for Examination of Liquids and Liquid Interfaces***, **Zihua Zhu***[1]*, Y Zhang,* Pacific Northwest National Laboratory **INVITED**

Secondary ion mass spectrometry (SIMS) has proven to be a powerful surface analysis tool, because it can provide elemental, isotopic and molecular information with excellent sensitivity and decent spatial resolution. However, SIMS is a high vacuum technique, and it normally is used to analyze solid samples. In recent years, in situ liquid SIMS was developed in my lab with collaboration with Dr. Xiao-Ying Yu, allowing molecular examination of various liquids and liquid interfaces. In brief, an interesting liquid can be sealed within a vacuum compatible device, and a thin silicon nitride (SiN) membrane is used to separate the liquid from vacuum. Then, we use a focused primary ion beam to drill an aperture through the SiN membrane to expose the liquid for SIMS examination. The key design of this idea is the diameter of the aperture: if the diameter is less than 2-3 microns, surface tension of the liquid can hold the liquid without any spraying out. Also, the evaporation from the aperture is controllable, making SIMS measurements fully feasible. If using a cluster primary ion beam, molecular signals from liquid surfaces and solid-liquid interfaces can be readily collected. In situ liquid SIMS has been used to investigate electrode-electrolyte interfaces during electrochemical or electro-catalytic reactions. The uniqueness of this novel approach is simultaneous collection of molecular evolution information of electrode surfaces, reactants, intermediates, and products under operando conditions, offering the possibility to elucidate complicated chemistries occurring at electrode-electrolyte interfaces (e.g., solid-electrolyte interphase in lithium ion batteries). More interestingly, the ionization process of in situ liquid SIMS may be softer than regular electrospray ionization, which is surprisingly different from the traditional opinion that SIMS ionization process is very hard with strong damage. This new finding will shed light on molecular investigation of ion solvation, nucleation before nanoparticle formation, and similar complex processes occurring in liquid environments.

[1] **ASSD Peter Sherwood Award**

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