

# Wednesday Afternoon, November 1, 2017

Vacuum Technology Division

Room: 20 - Session VT-WeA

## The History and Future of Materials, Surfaces and Interfaces (ALL INVITED SESSION)

**Moderators:** Gregory Exharos, Pacific Northwest National Laboratory, Amy Walker, University of Texas at Dallas

2:20pm **VT-WeA1 The 14-billion Year History of the Universe Leading to Modern Materials Science, Joe Greene,** University of Illinois **INVITED**

The story of our universe begins approximately 13.8 billion years ago with the Big Bang. Many of the formative events occurred in the first tiny fractions of a second (the universe evolved from consisting of a quark/gluon plasma to form the first protons and neutrons) to minutes (free neutrons decay to electrons and neutrinos) to a few tens of thousands of years (elementary particles form the first elements, which leads to the development of stars due to local density fluctuations). Planet Earth nucleated and began to accrete interstellar debris ~4.5 billion years ago. While the lighter metal elements on earth formed primarily due to stellar supernovae explosions, the primary mechanism leading to the formation of the heavier elements has only recently been demonstrated. The first known sophisticated stone tools used by hominids date to 2.6 million years ago.

Gold is likely the first metal discovered by man, >11,000 years ago. However, unlike copper (~9000 BC), bronze (~5000 BC), and cast iron (~600 BC), it was too soft for fabrication of tools and weapons. Instead, gold was used for decoration, religious artifacts, and commerce. The earliest high-purity Au artifacts derive from NE Bulgaria ~6500 y ago; however, the largest known concentration of ancient gold mines is in the Egyptian Eastern Desert. Copper extraction from ore was already being carried out in the Balkans (E Serbia and S Bulgaria) ~7500 years ago. Spectacular copper sculptures displaying very high levels of metallurgical and artistic craftsmanship have been found in Mesopotamia (S Iraq).

Gold brazing of metal parts was first reported ~3400 BC in Sumaria. The earliest documented thin films were gold layers, some < 1000 Å thick, produced by Egyptians ~5000 years ago. Examples, gilded on copper and bronze statues and artifacts (requiring sophisticated compositionally-graded interfacial adhesion layers), were found in pyramids dating to ~2650 BC. Electroless gold and silver plating was developed much later by the Moche Indians of Peru in ~100 BC.

Early biomaterials, used as human prosthetics following successful amputations, date to 950 BC in Egypt; while the first nano-based devices, exhibiting spectacular dichroic effects due to ~200-Å-diameter Au quantum dots, were synthesized in Rome ~350 AD.

Vapor-phase deposition of thin films required the invention of vacuum pumps (~1650 through 1865). The fascinating development of crystallography begins with Plato in 360 BC.

While an historical road map tracing the progress of materials technology is interesting in itself, the stories behind these developments are even more remarkable and provide insight into the evolution of scientific reasoning.

4:20pm **VT-WeA7 Controlling Microorganisms with Bio-inspired Materials, Caitlin Howell,** University of Maine

Nature was the first to create adaptive, multi-functional materials, surfaces, and interfaces. Now, the concept of borrowing ideas from Nature is one of the major drivers in the future of materials- and surface-based technology. In keeping with this trajectory, our group designs surfaces to understand and control microorganisms using bio-inspired concepts. One major application is in the control of bacterial adhesion leading to biofilm formation, which causes a wide range of problems in industry and medicine. Using a method inspired by the *Nepenthes* pitcher plant, which uses a thin immobilized layer of water to repel insects, we can create selective patterns of bacterial adhesion using common laboratory materials and simple bench-top surface treatments. Inspired by the vascular systems of plants and animals, we can then make these surfaces continuously self-replenishing by embedding channels within the material itself. The channels are then filled with excess liquid, which can diffuse to the surface and heal depleted or damaged areas. Finally, we are working to develop these materials on paper substrates to create low-cost, lightweight pathogen-handling materials for use in diagnostics or analytics. Through this work, we aim to develop new and versatile tools for the exploration and control of microorganisms.

4:40pm **VT-WeA8 Comparison of Oxygen Adsorption and Absorption on Rhodium, Silver, and Stepped Platinum Surfaces, Daniel Killelea, R.G. Farber, M.E. Turano,** Loyola University Chicago, *E.V. Iski,* University of Tulsa, *L.B.F. Juurlink,* Leiden Institute of Chemistry, The Netherlands, *J. Derouin,* Loyola University Chicago

The interaction of oxygen with the surfaces of catalytically active transition metals has attracted much interest because of the relevance to heterogeneous catalysis. Recently, we have shown that oxygen coverages in excess of 1 ML are achievable using gas-phase atomic oxygen (AO) to dose the metal surfaces. This talk will discuss some recent results comparing the uptake of AO and O<sub>2</sub> on Ag(111), Rh(111), and stepped Pt surfaces. On Pt surfaces, the geometry of the monoatomic steps determines whether or not low temperature dissociative chemisorption of O<sub>2</sub> will occur. In addition, on Pt(553), prolonged exposure to AO does not result in O coverages in excess of a monolayer, suggesting the defects are not effective at promoting the formation of subsurface oxygen. Conversely, on Rh(111), subsurface oxygen readily forms from exposure to AO. Finally, the uptake of oxygen on Ag(111) is discussed; unlike Pt(553) or Rh(111), where little surface reconstruction occurs, Ag(111) undergoes several phase transformations as the oxygen coverage is increased. These results using AO demonstrate that UHV-compatible dosing can prepare the same surfaces resulting high pressure O<sub>2</sub> exposures, allowing for quantitative and structural analysis of the oxidized surfaces.

5:00pm **VT-WeA9 Single Asperity Contact and Sliding, Ashlie Martini,** University of California Merced

Abstract: Nanoscale probes are widely used for surface and material characterization as well as for emerging nanoscale manufacturing techniques; they also are model single asperities and so provide a means of studying contact and relative motion between surfaces at a fundamental level. The challenge in understanding such phenomena is that experimentally-observed properties are determined by processes that occur within the interface between two materials. As such, it is desirable to complement experiments with simulations that can provide insight into the atomic-scale mechanisms within that buried interface. However, there are challenges to modeling nanoscale probe-based experiments with sufficient accuracy that the simulations can be used to explain experimental observables. We have addressed this issue in recent work by designing models to reproduce specific experiments in which nanoscale probes are used to characterize contact, friction and wear. We focus on tractable problems for which optimally-matched simulations can be directly validated by comparison to experiments and the simulations can in turn provide insight into the fundamental mechanisms underlying contact and sliding at the nanoscale.

5:20pm **VT-WeA10 Structure of Sub-nm Oxides Synthesized by Atomic Layer Deposition: From Isolated Cations to the Emergence of Crystallinity, Angel Yanguas-Gil,** Argonne National Laboratory

The history of the AVS has witnessed a dramatic reduction in thickness of thin film materials. Characteristic dimensions of the order of a nanometer are commonplace for a wide range of applications, from energy storage to semiconductor processing, nanostructured photovoltaics, catalysis or beyond Von Neumann computing architectures. This has greatly reduced our margin of error in terms of achieving the right microstructure and properties as well as the long-term stability of materials, particularly when the synthesis takes place at low temperatures and the mobility of surface species is low.

Atomic layer deposition is a thin film technique that is well known for its ability to coat high surface area materials, but it also allows us to grow materials with extremely high precision and high reproducibility. This makes it an ideal model system to understand some of the fundamental aspects of the growth of materials at the nanometer scale and their stability with time and under extreme environments. In this talk I will show how through the combination of different in-situ techniques, from PDF to XAFS and FTIR, the ability to modulate surface reactivity, simulation and theory, we can study the evolution of the structure of materials from isolated cations to a bulk-like structure and isolate the main factors driving the evolution of microstructure. Looking into the future, the development of new in-situ characterization tools at synchrotron radiation facilities worldwide is going to be an enabling capability that will help us understand the driving forces behind the emergence of crystallinity at low temperatures.

5:40pm **VT-WeA11 The Power of Atomic Layer Deposition – Moving Beyond Amorphous Films**, Virginia Wheeler, A.C. Kozen, B.P. Downey, M. Currie, N. Nepal, U.S. Naval Research Laboratory, L.O. Nyakiti, Texas A&M University, D.J. Meyer, D.R. Boris, S.G. Walton, C.R. Eddy, Jr., U.S. Naval Research Laboratory

Atomic layer deposition (ALD) has emerged as a powerful technique to produce a wide variety of thin film materials including metal oxides, nitrides, and metals for use in numerous applications. This method has become increasingly useful as device dimensions are reduced and complexity is increased often resulting in non-planar architectures. The sequential, self-limiting reactions that define ALD enable excellent conformality on high-aspect ratio structures, angstrom level thickness control, and tunable film compositions. Additionally, ALD is conducted at low growth temperatures ( $T_g$ ) which allows for integration of dissimilar materials as well as the ability to access new regions of phase diagrams in complex systems (ie. metastable phases, miscibility gaps, etc.). Traditionally, this low  $T_g$  yields amorphous films. In many applications, it is becoming increasingly advantageous to incorporate thin, conformal crystalline materials which are currently limited by the low  $T_g$  in ALD. To overcome this barrier, many have investigated post-deposition processing or plasma enhanced ALD. In this work, we will explore the advantages and limitations of approaches towards attaining crystalline ALD films through the following case studies: high quality phase transitions in ALD  $VO_2$  and phase control of heteroepitaxial  $Ga_2O_3$ .

$VO_2$  is a thermochromic material that undergoes a crystalline phase change at critical temperature ( $68^\circ C$ ) resulting in drastic changes in optical and electrical properties. While crystallized ALD  $VO_2$  films have been shown to have sufficient transitions, they are deposited amorphously. Crystalline films are only obtained through a post-deposition anneal ( $500-600^\circ C$  in  $O_2$ ) since the vanadium precursor degrades at elevated temperatures ( $>150^\circ C$ ). However, this high temperature anneal limits the integration of ALD  $VO_2$  films with other materials and without careful consideration of anneal parameters such as temperature, pressure and gas environment can alter the stoichiometry and structure of the initial ALD  $VO_2$  film.

A plasma enhanced ALD (PE-ALD) process was used to attain heteroepitaxial  $Ga_2O_3$  films on c-plane sapphire substrates at  $350^\circ C$ . This is about half of traditional CVD or MBE methods, showing the benefits of PE-ALD. Furthermore, the crystallinity and phase composition of the  $Ga_2O_3$  film can be control with growth temperature, plasma gas flow, and pressure. For example, reducing the chamber pressure an order of magnitude resulted in a shift from pure  $\beta$ - $Ga_2O_3$  to pure  $\alpha$ - $Ga_2O_3$  at low pressures. Initial results correlating plasma species with phase control will be presented and discussed as a way to overcome the limitations of the low ALD  $T_g$ .

6:00pm **VT-WeA12 The Cathodic Arc Plasma from Multi-Element Cathodes**, Robert Franz, Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

In the present work, the cathodic arc plasma from CrAl and NbAl composite cathodes is studied in detail. The ion energies are measured element, charge state and time resolved in vacuum conditions as well as in the presence of an inert and reactive background gas. Differences in the ion energy and charge state distributions between the plasma from the composite cathodes and corresponding single-element cathodes are noticed. Since it is expected that such differences originate from changes on the cathode surface, namely the formation of intermetallic phases, the erosion behaviour of the cathodes is also analysed. The latter is supported by density functional theory calculations providing additional information about the cohesive energy of the elements which includes the influence of surface texture and temperature. The presence of a background gas generally leads to a reduction of ion energies and charge states. Cathode poisoning effects are mainly observed outside of the main erosion zone. All obtained data are discussed on the basis of correlating the material properties of the cathodes and the plasma properties of the established discharges in order to obtain a comprehensive understanding of the cathodic arc discharge from multi-element cathode and to guide the further development of the deposition of thin films and coatings using such discharges.

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