

Advanced Surface Engineering Division Room 202C - Session SE+NS+TF-MoM

Nanostructured Thin Films and Coatings

Moderators: Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:20am SE+NS+TF-MoM1 The Role of Mechanical and Chemical Bonding Mechanisms in Adhesion of Nanoporous Anodic Aluminium Oxides (AAO), Shoshan Abrahami, Vrije Universiteit Brussel (VUB), Belgium; V.C. Gudla, Technical University of Denmark; K. Marcoen, Vrije Universiteit Brussel, Belgium; J.M.M. de Kok, Fokker Aerostructures; T. Hauffman, Vrije Universiteit Brussel, Belgium; R. Ambat, Technical University of Denmark; J.M.C. Mol, Technical University Delft, Netherlands; H. Terryn, Vrije Universiteit Brussel, Belgium

Anodic aluminum oxides (AAOs) are important nanostructures in many engineering applications. But despite their popular use, the important parameters that control their (dis-)bonding to an organic coating are not fully understood. This study uses an original approach that employs porous- and barrier AAO specimens for both chemical characterization and mechanical tests, thereby enabling the distinction between chemical and morphological contributions to the surface affinity for interfacial bonding. A validation for the cooperative effect of mechanical and chemical bonding mechanisms is given in this study. This was achieved by post-anodizing immersion of AAO's in sodium fluoride solution after anodizing in sulfuric acid (SAA) or a mixture of phosphoric- and sulfuric acid (PSA). Transmission electron microscopy (TEM) cross-section images show that fluoride-assisted dissolution smoothed the oxide surface, removing the fibril-like top nanostructure of the porous oxides, which are important for dry adhesion. However, chemical surface modifications were dependent on the initial oxide composition, as measured by X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Chemical analysis reveals that the surface hydroxyls of AAO are partially replaced by fluorides that do not form interfacial bonding with the epoxy resin. As a result, the peel strength of SAA under wet conditions is severely reduced due to these chemical changes. Conversely, fluoride-assisted dissolution of surface phosphates in PSA compensates for the adsorbed fluorides and the wet peel strength of PSA panels is not further deteriorated.

[1] S.T. Abrahami et al., J. Phys. Chem. C, 119, 19967-19975 (2015).

[2] S.T. Abrahami et al., npj Materials Degradation, 1, 8 (2017).

[3] S.T. Abrahami et al., J. Phys. Chem. C, 120, 19670-19677 (2016).

9:00am SE+NS+TF-MoM3 Two-dimensional Hexagonal Boron Nitride (hBN) Layer Promoted Growth of Highly-oriented, Trigonal-structured Ta₂C(0001) Thin Films via Ultra-high Vacuum Sputter-deposition on Al₂O₃(0001), Koichi Tanaka, P. Arias, M.E. Liao, Y. Wang, H. Zaid, A. Aleman, M.S. Goorsky, S. Kodambaka, University of California, Los Angeles

It is generally believed that single-crystalline substrates with either the bulk or surface structure and lattice constant identical or similar to that of the film being deposited are required for the growth of high-quality crystalline thin films. Recent studies have shown that deposition on van der Waals (vdW) layers can lead to highly-oriented thin films of a variety of crystal structures and lattice parameters. Here, we show that two-dimensional (2D) hexagonal boron nitride (hBN) layers ($a = 0.250$ nm and $c = 0.667$ nm) improve the crystallinity of trigonal-structured Ta₂C ($a = 0.310$ nm and $c = 0.494$ nm) thin films sputter-deposited on Al₂O₃(0001) substrates. Ta₂C layers of desired thickness ($t = 17 \sim 75$ nm) are grown on bare and hBN-covered Al₂O₃(0001) substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1327 K. hBN layers are deposited via pyrolytic cracking of borazine (~ 600 L) onto Al₂O₃(0001) substrates at 1327 K. The as-deposited Ta₂C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and transmission electron microscopy (TEM) based techniques. ω -2 θ XRD scans acquired from both Ta₂C/Al₂O₃(0001) and Ta₂C/hBN/Al₂O₃(0001) films with $t = 17$ nm exhibit only Ta₂C 0002n reflections (corresponding to $c = 0.494$ nm) while thicker layers ($t = 75$ nm) reveal the presence of additional 10 1 reflections. However, the 0002 reflection peak intensities are 5.4-fold stronger for the Ta₂C layers on hBN/Al₂O₃(0001) than bare Al₂O₃(0001). High-resolution TEM images and associated Fourier transforms indicate that the layers are single-crystalline. XRD ϕ scans show six 60°-rotated 1 0 - 1 2 peaks of Ta₂C at the same ϕ angles for 1 1 - 2 6 of Al₂O₃ based on which

we determine the epitaxial crystallographic relationships between the film and the substrate as Ta₂C(0002) || Al₂O₃(0006) with in-plane orientation of Ta₂C[1 0 -1 0] || Al₂O₃[1 1 -2 0]. We further show that 0002-oriented Ta₂C thicker films can be obtained by inserting hBN layers at regular intervals during the deposition of thicker Ta₂C films.

9:20am SE+NS+TF-MoM4 Nitride High Entropy Alloy Thin Films Deposited by Magnetron Sputtering and Cathodic Arc on Polymer Substrates: Structure and Electro-Mechanical Properties, Ao Xia, Montanuniversität Leoben, Austria; R. Dedoncker, Ghent University, Belgium; M.J. Cordill, Erich Schmid Institute of Materials Science, Austria; D.J.M.G. Depla, Ghent University, Belgium; R. Franz, Montanuniversität Leoben, Austria

In recent years a new class of materials has emerged in the field of metallurgy: high entropy alloys (HEAs). These metallic alloys consist of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as strength, ductility, corrosion resistance, wear resistance, hardness, diffusion and thermal conductivity. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

The focus of this report lies on the synthesis of MoNbTaVW HEA thin films by two different physical vapor deposition techniques, magnetron sputtering and cathodic arc deposition. The films were synthesized in Ar/N₂ atmosphere with varying gas flows in order to study the influence of N addition on structure and properties of the HEA thin films. Analysis by X-ray diffraction revealed a phase change from body-centered cubic (bcc) in case of the metallic HEA films to face-centered cubic (fcc) for the nitrides. A slightly lower N₂ gas flow is necessary in the case of magnetron sputter deposition to trigger the phase change than in the case of cathodic arc deposition. However, in both cases an increase in hardness was observed. For example, in the case of the films deposited by cathodic arc, the hardness increased from 18 to 30 GPa with the change from bcc to fcc phase. To further characterize the mechanical and electrical properties, the films were deposited on polymer substrates. The adhesion energy as determined from the geometry of buckles formed on the surface due to compressive stresses was a few J/m². In-situ uniaxial tensile tests revealed a brittle behavior of all films with crack onset strains of up to 3 %. The formation of elongated through thickness cracks caused a rather abrupt increase of the resistivity upon the crack appearance.

9:40am SE+NS+TF-MoM5 Isomeric Phase Composition and Mechanical Properties of NbN Nanocomposite Coatings Deposited by Modulated Pulsed Power Magnetron Sputtering, Y.G. Li, H. Yuan, Z.T. Jiang, N. Pan, M.K. Lei, Dalian University of Technology, China

Isomeric NbN nanocomposite coatings on stainless steel substrate with face-centered cubic phase δ -NbN and hexagonal phase δ' -NbN were deposited by modulated pulsed power magnetron sputtering under nitrogen flow rate f_{N_2} from 15% to 30%. It was found that the nitrogen flow rate f_{N_2} had a significant influence on the energy delivered in each macropulse, which led to a marked change in the phase composition and mechanical properties. The peak power decreases from 54 kW to 16 kW as f_{N_2} increases from 15% to 30% with the energy delivered in each macropulse from 23.2 J to 9.8 J. When f_{N_2} is at 15%, NbN coatings are mainly composed of δ' -NbN phase which usually exists at high f_{N_2} or under high compressive residual stress showing (100) and (102) preferred orientation, while δ -NbN gradually appears with the preferred orientation from (111) to (200) as f_{N_2} increases accompanied with the decrease of δ' -NbN phase composition. The hardness and modulus of isomeric NbN nanocomposite coatings go up to 36 GPa from 30 GPa and 460 GPa from 366 GPa as f_{N_2} increases to 20% with residual compressive stress from 0.47 GPa to 1.93 GPa, then decrease to 29 GPa and 389 GPa with residual compressive stress of 1.01 GPa showing a nonlinear response with peak power. The NbN nanocomposite coatings with more δ' -NbN phase show higher hardness and better toughness due to the composition variation of δ' -NbN and δ -NbN phases. The phase composition from δ' -NbN to δ -NbN phase should attribute to the delivered energy difference by peak power, and the anomalous increase in hardness should be originated from strengthening of the nanocomposite structure.

10:00am SE+NS+TF-MoM6 Ab initio Guided Development of Ternary Borides: A Case Study of Ti-B-N, Ti-Zr-B, Ti-W-B, Ta-W-B, and V-W-B Systems, V. Moraes, R. Hahn, M. Bartosik, H. Riedl, TU Wien, Austria; H. Euchner, Ulm University, Austria; D. Holec, Montanuniversität Leoben, Austria; Paul Heinz Mayrhofer, TU Wien, Austria

Transition-metal borides are a special class of ultra-high temperature ceramics. Among these, refractory borides such as TiB₂, ZrB₂, VB₂, TaB₂, and

Monday Morning, October 22, 2018

WB₂ are attractive candidates for many applications – ranging from high temperature electrodes, cutting tools, and molten metal containment to microelectronic buffer layers – because of their thermomechanical and chemical properties, their high melting temperatures up to ~3500 °C, and excellent high temperature strengths. However, these diborides have a comparably low fracture toughness of $K_{IC} \sim 1 \text{ MPa}\sqrt{\text{m}}$ (here, basically obtained by in-situ micromechanical cantilever bending tests).

How diboride materials can be designed – implementing quantum chemistry guided materials design concepts – to allow for a combination of high strength, ductility, and thermal stability, is the focus of this talk. We will use recent developments of diborides – where we applied alloying and architecture concepts (e.g., composition and/or phase modulated layers) – to explore such materials-science-based guidelines for improved properties. Especially the phase stability (with respect to chemistry and temperature) of diborides is an extremely interesting task. For example, only WB₂ (among all binary diborides, except for TcB₂) provides a G/B ratio below 0.5 (~0.34) and a positive Cauchy pressure $C_{13}-C_{44}$ (~73 GPa), which are typical indications for dominating non-directional bonds and thus a more ductile behavior. But WB₂ provides these properties only in its metastable α -structure (AlB₂-prototype) and not for its thermodynamically stable ω -structure (WB₂-prototype). With the help of ternary diborides, such as (Ti,W)B₂ or even (Ta,W)B₂, the α -structure can be stabilized (even up to ~1200 °C). Even more important is a selective sensitivity of the α - and the ω -structure for the formation of vacancies. Especially, when using physical vapor deposition (PVD) techniques at moderate temperatures (here ~400 °C) the content of vacancies (and point defects in general) is rather high. Such defects are less penalized in the α - than in the ω -structure, allowing for growing even single-phased α -WB₂ by PVD, exhibiting hardnesses H of ~40 GPa combined with high fracture toughness of $K_{IC} \sim 3 \text{ MPa}\sqrt{\text{m}}$.

With the help of superlattices, nanocolumnar and nanocomposite structures, we show that also with architectural concepts, strength ($H \sim 45 \text{ GPa}$) and ductility ($K_{IC} \sim 3.5 \text{ MPa}\sqrt{\text{m}}$) can be improved simultaneously.

The individual concepts will allow designing materials to meet the ever-growing demand for further improved coatings, tailor made for specific applications.

10:40am **SE+NS+TF-MoM8 Toughness Enhancement in Hard Ceramic Films by Alloy Design**, *Hanna Kindlund*, Department of Mechanical and Aerospace Engineering, University of California Los Angeles (UCLA) **INVITED** Transition-metal nitrides are refractory ceramics with high hardness, excellent wear resistance, high temperature stability, and good chemical inertness. Therefore, they are attractive in many applications, especially, as protective coatings against scratches, erosion, corrosion, and wear.

Tremendous efforts have been dedicated in enhancing hardness of ceramic films. However, in addition to high hardness, most applications also require high ductility, to avoid brittle failure due to cracking when coatings are subjected to high thermo-mechanical stresses. However, transition-metal nitrides, as most ceramics, are usually brittle, exhibiting low ductility and hence poor toughness.

Enhancing toughness in ceramic films is a challenging task that requires a fundamental understanding of the mechanical behavior of materials, which depends on their microstructure, electronic structure, and bonding nature. Theoretical studies using *ab initio* calculations predicted that alloys of VN with WN or MoN exhibit enhanced toughness as a result of their high valence electron concentrations, leading to an orbital overlap which favors ductility during shearing.

Here, I present experimental results on the growth of $V_{1-x}W_xN_y$ and $V_{1-x}Mo_xN_y$ alloy thin films, their microstructure, mechanical properties and electronic structure, and relate these properties with their enhanced ductility, demonstrating that it is possible to develop hard-yet-ductile ceramic coatings.

Advanced Surface Engineering Division Room 202C - Session SE-MoA

New Challenges and Opportunities in Surface Engineering

Moderators: Robert Franz, Montanuniversität Leoben, Austria, Jianliang Lin, Southwest Research Institute

1:20pm SE-MoA1 From Passive to Active Optical Coatings - Challenges and Opportunities for Pulsed Plasma Deposition Processes, *Ludvik Martinu*, Ecole Polytechnique de Montreal, Canada **INVITED**

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective (AR) coatings found in most optical components and low emissivity windows in buildings and automobiles to narrowband optical interference filters used in telecommunications. As the range of applications of OCs continuously broadens and extremely attractive market opportunities arise, it is becoming increasingly important to develop new nanostructured thin film materials with specific multifunctional properties. Further progress in this fast evolving field is strongly stimulated by a simultaneous action of two forces: a) the “pulling force” represented by the economic, technological and societal needs, including sustainable development, and b) the “pushing force” related to the curiosity-driven nanotechnology combining new design concepts of materials and devices, fabrication processes and innovative characterization tools, where the only limitation frequently appears to be our imagination.

This presentation will describe a holistic approach to OCs based on a broad and in depth knowledge of the interplay between the design, material, process and performance assessment with respect to specific applications and coating system durability in demanding environments. It will review the progress and future opportunities for the use of discrete, graded, and nanostructurally-controlled architectures benefiting from the nanomaterials’ meta-structures, advanced deposition techniques including high power impulse magnetron sputtering (HiPIMS) and tailored plasma- and ion-surface interactions, as well as complex systems implementing active (smart, tunable) materials.

Tomorrow’s trends will be illustrated by examples from different fields of applications ranging from passive hybrid elastic OC for ophthalmic lenses, hard protective OC for displays, and optical interference filters for gravitational waves detection to active OC and advanced glazings for energy saving using smart windows, active color-shifting security and authentication devices, and smart radiators with self-tuned emissivity for the thermal management in satellites.

2:00pm SE-MoA3 Anomalous Orientation-dependent Slip during Uniaxial Compression of TaC Crystals, *M. Chen*, ETH Zurich, Switzerland; *D.G. Sangiovanni*, Ruhr-University Bochum, Germany and Linköping University, Sweden; *A. Aleman*, *H. Zaid*, University of California at Los Angeles; *J.M. Wheeler*, ETH Zurich, Switzerland; *G. Po*, *Suneel Kodambaka*, University of California at Los Angeles

Binary carbides of group IV-VI transition-metals are hard, stiff, and high-melting solids with excellent high-temperature mechanical and chemical stabilities and good resistance to wear, ablation, and corrosion. Recent studies suggest that cubic B1-structured group IV and V transition-metal carbides, ZrC and TaC, are not intrinsically brittle and that they can exhibit plasticity under compression. Here, we present our results obtained using a combination of *in situ* scanning-electron-microscopy-based uniaxial micro-compression tests and *ab initio* molecular dynamics simulations conducted on TaC crystals, along with density functional theory calculations and finite-element based modeling of discrete dislocation and crack dynamics. We find that the room-temperature mechanical behavior of TaC is highly anisotropic and the operating slip systems are not necessarily those expected based on their Schmid factor. We find that the room-temperature mechanical behavior of TaC is highly anisotropic with yield strengths as high as ~17 GPa for $\{100\}$ and as low as ~5 GPa for $\{110\}$ crystals. Interestingly, the operating slip systems are not necessarily those expected based on their Schmid factor. We attribute the observed behavior to the normal component of the applied forces (in the direction perpendicular to the slip), whose magnitude varies with the slip plane and the crystal orientation. This anomalous slip results in the activation of $\{100\}$ slip systems during uniaxial compression of $\{100\}$, $\{110\}$, and $\{111\}$ crystals and $\{110\}$ slip systems in $\{111\}$ crystals and leads to the observed anisotropy in yield

strengths. We suggest that similar behavior should be expected in this class of materials.

2:20pm SE-MoA4 Selectable Phase Formation in Al-based Transition Metal Nitride Films by Controlling Al⁺ Subplantation depth during HIPIMS Deposition, *Grzegorz Greczynski*, Linköping University, Sweden; *S. Mraz*, *M. Hans*, RWTH Aachen University; *J. Lu*, *L. Hultman*, Linköping University, Sweden; *J.M. Schneider*, RWTH Aachen University, Germany

Alloying with Al is a common strategy to improve thermal and chemical stability of transition metal nitride (TMN) coatings deposited by magnetron sputtering. The solubility of Al in rock-salt-structure TMNs is, however, limited which presents a great challenge to increase Al concentration substantially, while avoiding precipitation of thermodynamically-favored wurtzite-AlN phase (*w*-AlN), which is detrimental to mechanical properties.

We present a novel thin film deposition method, which allows for unprecedented control over the phase formation in metastable TMN layers. The technique relies on hybrid high power impulse/dc-magnetron co-sputtering (HIPIMS/DCMS) of elemental targets in Ar/N₂ gas mixture with precise synchronization of the substrate bias pulse to the Al⁺-populated portion of the HIPIMS discharge which is superimposed onto a continuous TM neutral flux supplied from a DCMS-operated target. This results in a separation of film-forming species in time and energy domains and enables us to overcome the limitations of the conventional processing where phase formation is to large extent determined by the high adatom mobility and gas-ion-induced mixing, both taking place at the very surface, which drive the system towards thermodynamic equilibrium.

To demonstrate versatility of this technique we grow three series of high-Al-content films, namely Ti_{0.28}Al_{0.72}N, V_{0.26}Al_{0.74}N, and Zr_{0.48}Al_{0.52}N, all as a function of the amplitude of the synchronized bias pulse, which corresponds to varying the incident energy of Al⁺ ions E_{Al^+} . For all materials systems, the crystalline phase content is a very sensitive function of E_{Al^+} and can be tuned from completely hexagonal in the limit of low E_{Al^+} values (≤ 60 eV) to pure cubic obtained with $E_{Al^+} \geq 250$ eV. A complete transition from hexagonal *w*-AlN to supersaturated cubic NaCl structure is a consequence of the fact that the subplantation depth of Al⁺ metal-ions increases with increasing E_{Al^+} , as supported by Monte Carlo TRIDYN simulations. This innovative synthesis methodology enables unprecedented control over the phase formation and, hence, film properties and opens novel scientific avenues.

2:40pm SE-MoA5 Metallic-Glass Nanotube Arrays: A Novel Device for Various Applications, *Jinn P. Chu*, *J.K. Chen*, *C.C. Yu*, National Taiwan University of Science and Technology, Taiwan, Republic of China **INVITED**

A new group of thin film metallic glasses have been known to exhibit properties different from conventional crystalline metal films, though their bulk forms are already well-known for properties such as high strength because of their amorphous structure. We successfully fabricated the first-ever metallic glass nanotubes (MGNTs) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter, shown in Figure 1 [1]. The MGNT surface becomes hydrophobic, repelling water. By heating and cooling the array, water can be repelled and attached to the surface [1]. There are two examples presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. The detection limit of the arrays for streptavidin is estimated to be 25 nM, with a detection time of 10 min. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Second, the array is prepared on a heating device on Si and, with an applied electric voltage to the heating device underneath, the array surface was heated to generate an extending force from these nanochambers so that the array are functioned as biomimetic artificial suckers for thermally adhesion response in biological systems [3].

References

- [1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, *Materials Today*, 21 (2018), 178-185.
- [2] W. T. Chen, S. S. Li, J. P. Chu, K. C. Feng, J. K. Chen, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance, *Biosensors and Bioelectronics*, 102 (2018), 129-135.

Monday Afternoon, October 22, 2018

[3] W. T. Chen, K. Manivannan, C. C. Yu, J. P. Chu and J. K. Chen, Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass, *Nanoscale*, 10 (2018) 1366-1375.

3:40pm **SE-MoA8 Biocompatibility and Antibacterial Behaviors of TaON(porous)/TaN/TaN-Ag/Ta Multi-layered Thin Films**, *Joe. H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China; *C. Li*, National Yang Ming University, Taiwan, Republic of China; *C.C. Hsu*, Ming Chi University of Technology, Taiwan, Republic of China

In this study, a triple-layered thin film structure was designed and fabricated in order to realize porous and tunable TaOxNy thin films with enhanced biocompatibility and antibacterial behavior. In the design of film structure, the top layer was made of porous and tunable TaOxNy. The porous structure was obtained from TaOxNy-Cu (>50 at.%) thin films deposited by reactive sputtering. After the film was annealed by using RTA (1st annealing), the Cu phase was etched away to form TaOxNy network structure. The bottom layer was TaN-Ag (11 at.%) which is used as a Ag source layer. It also provided toughness and hardness. A thin TaN film was inserted between porous TaOxNy layer and solid TaN-Ag layer, and used as Ag diffusion control layer. The function of this layer was to withstand the 1st annealing, then, during the 2nd annealing, to let certain amount of Ag diffusive to the porous TaOxNy layer, and formed Ag nanoparticles. The films fabricated based on this design were studied systematically on their mechanical properties, Ag particle formation, as well as pore size and morphology. Finally, antibacterial property and biocompatibility of these films were studied in terms of O/N ratio, dealloying process, and Ag diffusion control. The relationships among O/N ratio, Ag nanoparticle formation, porosity, and bio-reactions will be discussed and reported systematically.

4:00pm **SE-MoA9 Electrochemically Deposited Coating with Antibacterial Properties against the Spread of Health Care-associated Infections**, *Nicole Ciacotich*, Technical University of Denmark, Denmark; *J.B. Rasmussen*, Elplatek A/S, Denmark; *K.N. Kragh*, University of Copenhagen, Denmark; *P. Møller*, *L. Gram*, Technical University of Denmark, Denmark

Health care-associated infections (HCAIs) are one of the major causes of patient morbidity during hospitalization. Most, if not all, HCAIs are the consequence of proliferation and transmission of pathogenic microorganisms in hospitals, especially in intensive care units. In addition, a range of items and devices, including hospital furniture (bedrails, frames, door handles) are fomites that often have a high load of pathogenic agents.

In a previous study, we developed an electroplated copper-silver alloy as antibacterial coating on stainless steel to minimize adhesion and transfer of pathogenic bacteria on environmental surfaces. We have characterized the electroplated copper-silver alloy in its microstructure, chemical and electrochemical nature and demonstrated a pronounced antibacterial activity.

The purpose of the present study was to evaluate the antibacterial efficacy in a standardized surface adhesion tests against *Staphylococcus aureus* 8325. We determined the influence of chlorine and phosphorus compounds, well-known complexing agents of copper common in hand sweat and surface detergents, by comparing the antibacterial effect of stainless steel, silver, copper and copper-silver alloy. In presence of phosphates and chlorides, the copper-silver coating showed the highest antimicrobial efficacy followed by copper, compared to stainless steel and silver. In absence of chlorides, there was no statistically significant difference among the different metal surfaces.

We also demonstrated that the antibacterial effect of the copper-silver alloy was considerably reduced if the direct contact between surface and bacteria, but not the passage of ions, was prevented. This suggests that the antibacterial action is mainly due to the so-called contact killing mechanism, which is distinctive of metallic copper, rather than the release of copper ions.

Furthermore, we performed confocal microscopy of bacteria on copper-silver coated surfaces using a modified live/dead staining in order to follow over time the bacterial killing front at the surfaces. This demonstrated, as the assays based on counting, a rapid killing spreading upwards in the bacterial biofilm within 30 minutes.

In conclusion, we believe that the electroplated copper-silver coating can be an effective instrument limiting spread of pathogenic microorganisms causing HCAIs in hospitals and intensive care units.

4:20pm **SE-MoA10 Tunable Self-Healing Thermal Barrier Coatings**, *S.S. Joshi*, *J.J. Gu*, *Y.-S. Ho*, *B.W. Wei*, *T.Y. Hung*, *Y.Y. Liu*, *N.B. Dahotre*, *S.M. Aouadi*, University of North Texas

Oxide ceramics exhibit a wide spectrum of unique properties, but can suffer from unpredictable and often catastrophic crack propagation and fracture, which limits their use in some applications. One possible solution to overcoming this limitation is to leverage the ability of oxides to repair their inherent flaws and cracks, i.e. to self-heal. The aim of the work is to gain new insights into self-healing mechanisms of a subset of ceramic surfaces, namely thermal barrier coatings, in response to thermal stimuli. TBCs are extensively used to protect metallic blades in gas-turbine engines against harsh operating conditions that include elevated temperatures and corrosive environments. Model systems that were investigated include YSZ-Al₂O₃-SiC and YSZ-Al₂O₃-TiC laser processed coatings. The healing process occurs when the carbide phase oxidizes and the resulting oxide flows to the crack site and bonds to the YSZ matrix. The formation of the oxide phase was observed using X-Ray diffraction its formation in the crack site was confirmed using cross-section scanning electron microscopy. The optimum process to create a self-healing composite was determined. Finally, the mechanisms responsible for how the self-healing process impacts deformation and failure resistance as well as corrosion resistance at elevated temperatures was investigated.

Plasma Science and Technology Division Room 104A - Session PS+EM+SE-TuM

Plasma Processing of Challenging Materials - I

Moderators: Necmi Biyikli, University of Connecticut, Jun-Chieh Wang, Applied Materials

8:00am **PS+EM+SE-TuM1 Development and Understanding of Isotropic Etching Process of Si Selectively to Si_{0.7}Ge_{0.3}**, *Sana Rachidi, A. Campo, V. Loup, CEA-LETI, France; N. Posseme, CEA, LETI, France; J.M. Hartmann, S. Barnola, CEA-LETI, France*

The vertically stacked wires MOSFET architecture pushes further the scaling limits of the CMOS technology. Now deemed as a possible extension to FinFET, it offers multiple benefits. A low IOFF current is indeed expected, thanks to multi-gate electrostatic control, with a high current drivability due to 3D vertically stacked channels.

The fabrication starts with the epitaxial growth of (Si_{0.7}Ge_{0.3}/Si) multilayers (8-12 nm for Si and SiGe layers) on blanket SOI substrates. Then, individual and dense arrays of fins were patterned to fabricate stacked-NWs FETs with 40 nm-pitch fins which are 36 nm high and roughly 20 nm wide. After that, dummy gates and spacers are defined prior to the anisotropic etching of the (Si/SiGe) multilayers. Today one of the most critical step in such device realization is the isotropic silicon removal selectively to silicon germanium.

In this study an understanding of selectivity evolution between Si and SiGe as a function of CF₄/O₂/N₂ remote plasma parameters is presented. The experiments performed on 300mm blanket wafers (Si and Si_{0.7}Ge_{0.3}) have been carried out on CDE-Allegro.

The impact of etching parameters (CF₄, O₂, N₂, microwave-power, pressure and temperature of the electrostatic chuck) and different pre-treatments on etching rates and selectivity is first investigated. X-ray photoelectron spectroscopy (XPS) analyses will show that for Silicon, a SiO_xF_y thick reactive layer is formed on the etched surface and controls its etching regime. As for Si_{0.7}Ge_{0.3}, a passivation layer of 2 nm is observed. And it contains a mixture of GeO_x and SiO_xF_y species.

Based on these results, application to patterned wafers will be shown. Scanning Electron Microscopy (SEM), Transmission electron microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX or EDS) are here used for the pattern characterisation.

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8:20am **PS+EM+SE-TuM2 III-V/Ge Heterostructure Etching for Through Cell Via Contact Multijunction Solar Cell**, *Mathieu de Lafontaine, G. Gay, C. Petit-Etienne, E. Pargon, LTM, Univ. Grenoble Alpes, CEA-LETI, France; M. Darnon, A. Jaouad, M. Volatier, S. Fafard, V. Aimez, 3IT, Univ. de Sherbrooke, Canada*

Through cell via contact architecture aims to increase the multijunction solar cell efficiency by 3% and the power yield per wafer by 20% by transferring the front side contact to the backside using insulated and metallized vias. Via hole plasma etching through the III-V/Ge heterostructure is a key step to fabricate this new architecture. It is challenging, as dozens of layers must be anisotropically etched with low roughness and free damage to ensure optimal cell performance. Moreover, etched patterns must have a depth of >30 μm and present >3 aspect ratio. In this abstract, several patterning strategies are presented to address these challenges.

The epiwafers consist of a 8μm-thick III-V heterostructure (InGaP, InGaAs, GaAs, AlInP, AlGaAs, AlGaInP layers and quantum dots) epitaxially grown on Ge substrate. A 5μm thick SiO₂ hard mask (HM) is first deposited by PECVD and patterned by contact photolithography and plasma etching. The optimization of both the lithography and HM opening steps is crucial for an optimal transfer into the III-V/Ge layers. It is observed that sloped and rough hard mask sidewalls after the HM opening step are detrimental to the via hole etching and lead to severe damage on the heterostructure sidewalls. Combining a thick photoresist mask with vertical sidewalls and an optimized Ar/C₄F₈/O₂ plasma process developed in a capacitive coupled plasma reactor allows to pattern the 5μm-thick HM with vertical and quite smooth sidewalls.

A room temperature SiCl₄/Cl₂/H₂ plasma process was developed in an inductively coupled plasma reactor to etch vias in the III-V/Ge heterostructures. The cell performance loss associated to via etching was
Tuesday Morning, October 23, 2018

almost absent, indicating that such chemistry is suitable for photovoltaic applications. However, some layers present isotropic etching, which is problematic for the via insulation and metallization. Indeed, III-V compounds with low indium concentration are more sensitive to lateral etching, thus creating preferential isotropic etching in several III-V layers. This represents a challenge considering the aspect ratio and the depth targets. Indeed, lateral etching will be even greater for a longer process time. To obtain anisotropic etching, a high temperature (200°C) SiCl₄/Cl₂/H₂ process is proposed. The enhanced volatility of the indium by-products combined with the Si-based passivation could improve the anisotropy while maintaining optimal cell performance. FIB-TEM and EDX are performed to characterize both the etch morphology and the passivation layer. Moreover, optoelectrical measurements will assess the cell performance after via etching.

8:40am **PS+EM+SE-TuM3 Feature Scale Modeling of Etching of High Aspect Ratio Silicon Structures in Pulsed Plasmas**, *Wei Tian, J.-C. Wang, S. Sadighi, J. Kenny, S. Rauf, Applied Materials*

As critical dimensions shrink below 7 nm, etching of high aspect ratio (HAR) Si structures, such as those used for shallow trench isolation (STI), is becoming challenging. Some strategies to deal with these challenges include multi-step cyclic processes and pulsed plasmas. In this paper, we consider a cyclic pulsed plasma process for Si etch. Etching is done by cycling three steps: oxidation (OX), Si main etch (ME) and clean. The OX step passivates the Si sidewalls and protects them during Si ME. Si is mainly etched during the ME step, where the ion energy and angular distribution (IEAD) and ion / neutral flux ratio are controlled through power pulsing. The clean step removes the Cl/Br-containing passivation from the Si surface prior to re-oxidation. Pulsed plasmas have demonstrated several advantages compared to continuous wave (CW) plasmas and have become indispensable in etching of the next generation of microelectronic devices [1-2]. When source power and/or bias power are pulsed, a variety of pulsing modes are possible. Pulsing duty cycles and phase shift provide additional knobs for controlling the etching characteristics. In order to understand the effects of pulsing modes on etching properties, a feature scale model coupled to a plasma model is desired.

In this work, we investigate several pulsing modes during the Si ME step including separate pulsing of the plasma source or bias powers, and their synchronized pulsing. Plasma models for the 3 steps including the pulsed plasma step [3] are coupled to a 3D Monte Carlo feature scale model. Process performance has been quantitatively evaluated by examining etch rates for Si and the SiO₂-like mask, Si/mask etch selectivity, and critical dimensions within the HAR features. When only the radio-frequency (RF) bias power is pulsed, Si and mask etch rates scale with pulse duty cycle. As a result, if Si is etched to the same depth, the HAR trenches are wider at higher duty cycles due to less total oxidation time and less protection of the sidewalls. Source power pulsing provides higher Si etch rate because of RF bias power being on continuously, but suffers from poor mask selectivity. Synchronized pulsing of both the source and RF bias powers in conjunction with phase control provides additional flexibility in modulating the IEAD and the ion/neutral flux ratio. RF bias pulsing and in-phase synchronized pulsing yield the best selectivity for the conditions explored.

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9:00am **PS+EM+SE-TuM4 Plasma Etching of High Aspect Ratio Oxide-Nitride-Oxide Stacks**, *S. Huang, C. Hurard, University of Michigan; S. Nam, S. Shim, W. Ko, Samsung Electronics Co., Ltd., Republic of Korea; Mark Kushner, University of Michigan*

Increasing demand for large memory capacity is now being met by 3-dimensional vertical structures. Fabricating these structures requires plasma etching through hundreds of stacked layers resulting in extremely high aspect ratio (up to 100) vias. The stack typically consists of alternately deposited silicon nitride and silicon oxide layers which serve as the sacrificial material and gate dielectric respectively. When combining the high aspect ratio (HAR) and hybrid materials, the etching of oxide-nitride-oxide (ONO) stacks faces both traditional (e.g., aspect ratio dependent etching, bowing and charging) and new challenges (e.g., mixing layers, line edge striation and tapered etch front through several layers).

In this paper, we report on results from a computational investigation of the etching of ONO stacks using tri-frequency capacitively coupled plasmas sustained in fluorocarbon gases. The reactor scale modeling was performed

Tuesday Morning, October 23, 2018

using the Hybrid Plasma Equipment Model (HPEM), from which the neutral and ion fluxes and ion energy and angular distributions (IEADs) to the wafer surface were obtained. The feature scale modeling was performed using the 3-dimensional Monte Carlo Feature Profile Model (MCFPM) with a newly developed polymer mediated fluorocarbon etching mechanism for oxide and nitride.

During the etching of ONO stacks, the etch front quickly evolves to a tapered profile at low aspect ratio (~5) and persists into deeper features, mainly due to re-deposition of sputtered fluorocarbon radicals within the feature. The etch rate generally decreases with increasing aspect ratio due to limited transport of radicals and ions. Conductance, ion reflection from sidewalls and charging all play of role in the flux of reactive species to the etch front. When the etching proceeds through the ONO stack, the etch rate fluctuates, becoming higher for the nitride and lower for the oxide. The formation of scalloping due to different lateral etch rates for each material is observed for some conditions while not for others. The mechanism behind this scalloping, and methods to minimize its effect will be discussed.

* Work supported by Samsung Electronics Co. Ltd, National Science Foundation and the Department of Energy Office of Fusion Energy Sciences.

9:20am **PS+EM+SE-TuM5 Etch Profile Evolution in Poly-silicon using Halogen Containing Plasmas for Next Generation Device Fabrication, Shyam Sridhar, S.A. Voronin, P. Biolsi, A. Ranjan**, TEL Technology Center, America, LLC

The shrinking and introduction of complex three-dimensional device structures poses a great challenge for plasma etching. With ever-decreasing feature pitches, it is extremely important to achieve a near ideal etch profile, i.e. vertical sidewalls and flat etch fronts. The challenges are manifold in etching three-dimensional structures. For example, in etching high aspect ratio square shaped holes, it is difficult to remove the targeted material from the corners, especially at the bottom of the feature.

In this work, we report the impact of process parameters such as ion energy, neutral and ion fluxes on the profile evolution of closely spaced poly Si lines using F, Cl, and Br containing plasmas. Etching in Cl and Br plasmas resulted in anisotropic profiles with bowed and tapered sidewalls. Addition of gases such as oxygen or fluorocarbons to minimize bowing resulted in enhanced tapering of sidewalls. The etch fronts were found to be relatively flat or curved depending on the ion energy. Micro trenching was also found to influence the shape of the etch front. We attempt to extend the learning from etching two-dimensional lines to three-dimensional features, in order to define a better processing space for new and emerging applications.

9:40am **PS+EM+SE-TuM6 Flux and Energy of Reactive Species Arriving at the Etch Front in High Aspect Ratio Features During Plasma Etching of SiO₂ in Ar/CF₄/CHF₃ Mixtures, Soheila Mohades**, University of Michigan; M. Wang, A. Mosden, TEL Technology Center America, LLC; M.J. Kushner, University of Michigan

Multi-frequency, capacitively coupled plasmas (CCPs) provide additional control in semiconductor processing by separating production of ion fluxes from acceleration of ions into the wafer. In dual-frequency capacitively coupled plasmas (DF-CCPs), the higher frequency (HF, tens to hundreds of MHz) sustains the plasma and the lower frequency (LF, a few to 10 MHz) controls acceleration of ions into the wafer. Although the goal is to have completely separate control, changing the frequency and power of the LF does affect the magnitude of reactive fluxes to the wafer in addition to the ion energy and angular distributions (IEADs). As the aspect ratio (AR) of features approaches 100 in high aspect ratio (HAR) etching of dielectrics, the parameter of interest is the flux of reactants that reaches the etch front, which is not necessarily the same as the fluxes that enter the feature. Issues such as side-wall scattering and neutral conductance in the feature modify those fluxes as the AR increases.

In this paper, the IEADs and reactive fluxes reaching the etch front during fluorocarbon plasma etching of SiO₂ were computationally investigated as a function of AR. The feature scale modeling was performed using a 3-dimensional implementation of the Monte Carlo Feature Profile Model (MCFPM). The IEADs and reactive fluxes incident onto the feature were obtained using the 2-dimensional Hybrid Plasma Equipment Model (HPEM). The parameter space for the DF-CCP has LF of a few to 10 MHz, HF of 40 MHz, with powers of 100-1000 W applied to the bottom electrode with and without a dc-augmented top electrode in a gas mixture of Ar/CF₄/CHF₃ at 10s of mTorr. The reactive fluxes and energies onto the etch

front for AR of up to 100 are discussed for ions, hot-neutrals and thermal neutrals.

* Work supported by TEL Technology Center, America, LLC, National Science Foundation and the Department of Energy Office of Fusion Energy Sciences.

11:00am **PS+EM+SE-TuM10 Wafer-scale Fabrication of Suspended Graphene Nanoribbon Arrays -from Growth Dynamics to Optoelectrical Applications-, Toshiaki Kato, T. Kaneko**, Tohoku University, Japan **INVITED** Graphene nanoribbons (GNRs) combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. However, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. We have developed a new, simple, scalable method based on novel plasma catalytic reaction [1-5] for directly fabricating narrow GNRs devices with a clear transport gap [6]. Since the establishment of our novel GNR fabrication method, direct conversion of a Ni nanobar to a suspended GNR is now possible. Indeed, GNRs can be grown at any desired position on an insulating substrate without any post-growth treatment, and the wafer-scale synthesis of suspended GNR arrays with a very high yield (over 98%) is realized [7]. The growth dynamics of suspended GNR is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. The improvement of thermal stability of Ni nanobar can be a key to realize the GNR nucleation in our method, which can be given by supplying higher density of carbon from plasma to liquid-phase Ni nanobar. The wettability of liquid-phase Ni nanobar against to the SiO₂ substrate is also found to be an important factor forming the suspended structure of GNR. It is also revealed that the minimum length of GNR can be decided by the wavelength of Plateau-Rayleigh instability known as a traditional instability of fluid flow. We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the optoelectrical applications [8-10] in industrial scale.

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11:40am **PS+EM+SE-TuM12 Investigation of Surface Reactions for GeSbTe-based Phase Change Material: From Etching to Final Sealing Process, Yann Canvel, S. Lagrasta**, STMicroelectronics, France; C. Boixaderas, S. Barnola, CEA-LETI, France; E. Martinez, CEA/LETI-University Grenoble Alpes, France

Chalcogenide phase-change materials (PCMs), such as Ge-Sb-Te (GST) alloys, have shown outstanding properties, which have led to their successful use for a long time in optical memories (DVDs) and, recently, in non-volatile resistive memories. The latter, known as PCM memories, are among the most promising candidates to be integrated into next generation smart-power and automotive applications [1].

Chalcogenide PCMs exhibit fast and reversible phase transformations between crystalline and amorphous structures with very different resistivity states. This distinctive ability to store the information gives a unique set of features for PCMs, such as fast programming, flexible scalability, high data retention and performing endurance [2][3].

In the perspective of large-scale integration, which means incorporation of the PCM into more and more confined structures, the device performances are getting increasingly more sensitive to surface effects of the GST layer. Thus, it is crucial to maintain a homogeneous stoichiometric composition in the GST surface/volume all along the manufacturing process, particularly during the patterning of PCM cells.

Tuesday Morning, October 23, 2018

In this study, we examine the main surface reactions that GST material must face and we illustrate how these reactions are likely to modify its composition.

In particular, we will focus on the surface damages generated by different halogen-based plasma etching processes [4][5]. An innovative etching method, compatible with extreme confined structures, will be highlighted.

Then, we will study the oxidation of GST, responsible of the critical surface degradation after the etching process [6]. According to the exposure conditions, the GST surface undergoes some specific chemical modifications that will be pointed out.

Finally, the stability of GST composition will be evaluated at each point of a standard GST patterning process: from etching to final sealing of PCM cells. It will allow us to understand how the chalcogenide material is degraded during the whole process. Some improvements will be exhibited in order to reduce this degradation.

Plasma etching were carried out in a 12 inch planar ICP reactor. And all the surface analyses were performed by using different techniques of material characterization, such as XPS, PP-TOFMS and EDS.

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12:00pm PS+EM+SE-TuM13 Behaviors of Charged Species in Afterglow of Dual Frequency Pulsed Capacitively Coupled Plasma with a Synchronous Negative DC-bias, Takayoshi Tsutsumi, T. Ueyama, K. Ishikawa, H. Kondo, M. Sekine, Nagoya University, Japan; Y. Ohya, Tokyo Electron Miyagi Limited; M. Hori, Nagoya University, Japan

Dual frequency pulsed capacitively coupled plasma with a synchronous negative DC-bias to a top electrode is developed for the improvement of high-aspect-ratio contact hole (HARC) fabrications. It enables to suppress the distorted etched profiles such as twisting. These distortions are due to the distortions of ion trajectories inside the deep contact holes, which are charged up positively. It is expected that charged species presented in early afterglow were neutralized on the surfaces in the holes. We focus on the behavior of charged species in the afterglow period of the synchronous negative DC-bias imposition to the top electrode in the pulsed dual frequency CCP.

For temporal change of electron density in the afterglow, the synchronous negative DC-bias resulted in lower decay rate of electron density in afterglow¹. The result indicate that higher DC-bias imposition causes more electron generation. Moreover, the decay rate near the bottom electrode is lower than that of near the top electrode. The possible explanation is electron generation or sustaining mechanism in the afterglow of DC synchronized pulsed plasma. We measured OES to confirm the electron generation or plasma sustainment in the afterglow. The intensities of Ar emission (at a wavelength of 750.38 nm) in afterglow decreased at the beginning of RF off period and increased after several μ s. This phenomenon was not observed in the constant DC-bias condition.

The synchronous DC-bias voltage seems to accelerate the positive ions to the top electrode. And ion bombardment to the top electrode surface enhance the generation of the secondary electron in the afterglow. We consider that this influence the generation of negative ions and the neutralization of the charged surface of the hole in afterglow.

¹T. Ueyama, Y. Fukuanga, T. Tsutsumi, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine, M. Iwata, Y. Ohya, H. Sugai, and Hori, Jpn. J. Appl. Phys. 56, 06HC03 (2017).

Advanced Surface Engineering Division

Room 202C - Session SE+PS-TuM

Plasma-assisted Surface Modification and Deposition Processes

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:00am SE+PS-TuM1 Surface Modification of 304 Stainless Steel by Neutral Nitriding, Petros Abraha, Meijo University, Japan

Austenitic stainless steel is the choice of material in the manufacturing industries for its corrosion resistance but lacks surface hardness leading to poor wear resistance and ultimately short lifetime. Stainless steel possesses the same microstructure at all temperatures and therefore, cannot be hardened by heat treatment. Attempts to increase the hardness of austenitic stainless steels by plasma nitriding has been successfully demonstrated in using different processes and methods. Here, we have introduced a nitriding method that improves the hardness and corrosion resistance of stainless steel while maintaining the initial surface conditions of the untreated surface.

In this research, neutral nitriding, a plasma nitriding method performed on a sample inside a cathodic grid in using an electron beam excited plasma device is presented. In this method, nitrogen ion incidence onto the sample surface is prevented by a positive bias to the sample ultimately controlling the formation of the compound layer. Further, the incidence of electrons causing an excessive rise in sample temperature is prevented by applying a negative bias to the cathodic grid. The setup creates a favorable condition that enables the neutral nitrogen species to be the primary species within the plasma to diffuse into the sub-surface of the sample and form a hardened layer.

The results obtained are as follows: (1) The S-phase without any compound layer on the surface was confirmed and the surface roughness of the untreated surface (R_a 10 nm) was maintained (R_a 15 nm). (2) The surface hardness was increased to more than two times, 550 Hv. (3) Pitting potential tests confirm Improved critical pitting potential on samples nitrided at 350 °C and 375 °C.

8:20am SE+PS-TuM2 Plasma Cratering and Hardening for Friction Reduction and Wear Resistance of Cast Iron, Wei Zha, University of Windsor, Canada; C. Zhao, X. Nie, University of Windsor, Canada

Cathodic plasma electrolysis (CPE) is used to reduce the friction and increase the wear resistance of cast iron. During the process, cast iron sample serves as a cathode where the plasma discharging occurs, increasing the surface hardness and leaving an irregular array of craters on the surface. As the applied voltage increases, the number and size of craters become larger. The areal density of craters (as reservoir) and oil retention are determined from SEM image analysis and surface profiler. Reciprocating tribotests are conducted on blank sample, CPE-treated samples and sample with crosshatched surface. The results show that the CPE-treated samples can have a lower coefficient of friction and higher wear resistance than other two kinds of samples. As for the CPE-treated samples, the friction behaviors are also discussed by considering effects from their areal density of craters, surface roughness and oil retention.

Keywords: Cathodic plasma electrolysis, Cratering, Hardening, Friction, Wear

8:40am SE+PS-TuM3 Area-selective Deposition by Surface Engineering for Applications in Nanoelectronics. From Blanket to Confined Dimensions, Silvia Armini, IMEC, Belgium

At advanced nodes targeting 10nm feature size and below, lithography starts to dominate costs (EUV, multiple mask passes per layer, pattern placement error). Complementary techniques and materials are needed to continue 2D scaling and extend the Moore's law. Area-selective atomic layer deposition (AS-ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. The strong sensitivity of ALD to the chemistry of the surface and its self-limiting nature are particularly appealing. In this talk we report two examples of AS deposition triggered by i) area activation, i.e. a H₂-based plasma triggered selective placement of ALD Ru catalyst on SiCN liner with respect to amorphous carbon materials (Fig. 1) followed by AS electroless metal bottom-up deposition and ii) area deactivation by a combination of surface functionalization by molecular self-assembled organic films and ALD of metal oxides and metal nitrides. In the latter case the idea is to chemically and locally bond a molecule directly to the metal surface in order to inhibit reactive sites and then prevent further reactions

Tuesday Morning, October 23, 2018

between the precursor molecules and the surface. A selectivity driven benchmarking of organic passivation films deposited on copper surface from the vapor and liquid phase will be presented, both on blanket surfaces, micron-scale and nanometer-scale patterned features. Two major challenges will be investigated: i) defectivity induced by a reactive ALD process which also nucleates on the part of the surface covered with the organics and metrology; ii) understanding and control of AS ALD material shape at the boundaries between Cu and dielectrics. In Fig.2 the top-down SEM images after AS ALD Hf nitride on 240nm Si oxide/50nm Cu lines are shown. A target thickness of 10nm Hf nitride is deposited by ALD at 120°C.

9:00am SE+PS-TuM4 Experimental and Numerical Evaluation of Cohesive and Adhesive Failure Modes during Indentation of TiAlN Coatings on Si(100) Deposited by MPPMS, Z.T. Jiang, M.K. Lei, Dalian University of Technology, China

The mechanical behavior of TiAlN coatings was studied by Indentation test and FEM modeling. The TiAlN coatings were deposited by modulated pulse power (MPP) magnetron sputtering. The peak power was used from 21 kW to 50 kW with the gas flow ratio of Ar/N₂=4:1. The microstructure of the indented regions was observed by focused ion beam (FIB), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD with grazing angle of incidence reveals that the coatings consisted with c-TiAlN. The achieved hardness and modulus for the coatings show significant increase from 23.6 GPa to 46.7 GPa and 396 GPa to 461 GPa. The eXtended Finite Element Method (XFEM) was applied to study the cohesive cracks through the coatings, while the Cohesive Zone Model (CZM) was to evaluate the coating/substrate interfacial crack. The stress transfer from the coating to the substrate was dependent on the elastic and elastic/plastic properties of the coating and substrate. The energy release rate of the coating and the cohesive zone parameters were investigated by the fracture toughness of the coatings. Compared with the experimental results, the simulation results were able to accurately observe the deformation as well as the fracture behavior of the coatings. Under indentation loading, the crack initiation tended to begin at the outer surface and to propagate along the coating in thickness direction until the cracks reached the substrate.

9:20am SE+PS-TuM5 Growth of TiB_x Thin Films by DC Magnetron Sputtering and High-Power Impulse Magnetron Sputtering: Effect of Pressure and Substrate Temperature, Niklas Hellgren, Messiah College; J. Thörnberg, I. Zhirkov, Linköping University, Sweden; G. Greczynski, Linköping University, Sweden; J.P. Palisaitis, Linköping University, Sweden; M. Sortica, Uppsala University, Sweden; P.O.A. Persson, Linköping University, Sweden; I. Petrov, J.E. Greene, University of Illinois at Urbana-Champaign; L. Hultman, J. Rosen, Linköping University, Sweden

We report on titanium boride, TiB_x, thin films grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB₂ target, in an attempt to grow high-quality stoichiometric TiB₂ films. The composition, microstructure, and texture was analyzed as a function of deposition temperature (room temperature – 900 °C) and pressure (5 – 20 mTorr). Films deposited by DCMS at low pressure, regardless of temperature, result in over-stoichiometric films (B/Ti ≈ 3), while high pressure gives close to stoichiometric films. This can be explained by differences in angular distribution of sputtered B and Ti atoms, as well as differences in gas scattering [1]. These high-pressure films, however, are under-dense and have a mixed 100/101 preferred crystal orientation.

The composition of the HiPIMS-deposited films show a more complex dependence on pressure and temperature: At low temperatures, the trend vs pressure is opposite to DCMS, with the higher pressure resulting in higher B/Ti ratio. At higher temperatures, the effect of pressure is smaller, and even reverses slightly, with higher pressure giving lower B/Ti ratio.

We attribute these trends to a combination of several factors: (1) The much higher degree of ionization in HiPIMS, and the different transport of the ionized sputtered particles in the presence of a magnetic field, (2) gas density decrease at higher temperature resulting in less scattering, and (3) more sublimation, primarily of boron, at higher substrate temperatures. The highest quality stoichiometric TiB₂ films, with 001-textured nanocolumnar structure, form by HiPIMS at 5 mTorr and 500-700 °C.

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9:40am SE+PS-TuM6 Time-resolved Analysis of the Cathodic Arc Plasma from Nb-Al Cathodes, S. Zöhrer, Montanuniversität Leoben, Austria; A. Anders, Lawrence Berkeley National Laboratory, Leibniz Institute of Surface Engineering (IOM), Leipzig, Germany; D. Holec, 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.

By using a time-resolved method in combination with pulsed arcs and a comprehensive Nb-Al cathode model system in this work, we investigate the influence of cathode composition on the plasma, while making the influence of neutrals visible for the observed time frame. This model system consists out of three different Nb-Al compositions with the atomic ratios 75/25, 67/33 and 25/75, as well as pure Nb and Al cathodes. The results visualize ion detections of 600 µs plasma pulses, extracted 0.27 m from the cathode, resolved in mass-per-charge, energy-per-charge and time. In addition to high vacuum at a base pressure of 10⁻⁴ Pa, the measurements were carried out at three elevated Ar gas pressures: 0.04 Pa, 0.20 Pa and 0.40 Pa. Ion properties were generally found to be strongly dependent on the cathode material in a way that cannot be deduced by simple linear extrapolation. For high vacuum, current hypotheses in cathodic vacuum arc physics applying to multielement cathodes, like the so called “velocity rule” or the “cohesive energy rule”, are tested for early and late stages of the pulse. In addition, the influence of an inert background gas is analysed by comparing the results with those at increased pressure, which show reduced ion charge states, up to a state where mostly Nb²⁺ and Al¹⁺ ions are detected. Beside Nb and Al ions, time-resolved energy and charge distributions of Ar ions are taken into account, providing further insights on the processes involved.

11:00am SE+PS-TuM10 Dedicated Experiments to Challenge a Model for Reactive Magnetron Sputtering, Diederik Depla, Ghent University, Belgium
INVITED

Reactive magnetron sputter deposition is conceptual easy technique which can be explained in a few lines. Behind this apparent simplicity there is a complex interplay between different plasma and surface related processes. To get a better understanding of the impact of the different process parameters, modelling is inevitable. Therefore, the paper will first focus on the RSD (Reactive Sputter Deposition) model. As this code is freely downloadable and it has a GUI, it permits not only the research team to investigate this fascinating deposition technique, but also you. Important target processes such as sputtering, chemisorption, direct and knock-on reactive ion implantation will be discussed. With the model as a guide, some important fundamental questions will be tackled. Experiments related to the transition from metallic to poisoned mode, the deposition rate during reactive sputtering, the presence of parameter hysteresis will be presented. The confrontation between model and experiment will highlight not only the success of the RSD model, but also the further challenges to improve this model, and our understanding of reactive magnetron sputtering.

11:40am SE+PS-TuM12 Current-voltage-time Characteristics of HiPIMS Discharges Revisited, André Anders, Leibniz Institute of Surface Engineering (IOM), Germany

Continuous discharges can be characterized by their current-voltage (*I-V*) characteristics, which expresses the quasi-steady-state plasma impedance for slowly varying parameters of the driving circuit. For fast and strongly changing conditions, the plasma impedance may become a strong function of time and therefore one needs to explicitly add time as a parameter, leading to current-voltage-time (*I-V-t*) characteristics .

This general approach is applicable to magnetron sputtering, where the magnetron's *I-V* characteristic is a power law, $I = K V^n$, with *K* being a device-specific constant and the power exponent *n* typically in the range from 6 to 10. For HiPIMS, the current is a strong function of time, and one needs to consider *I-V-t* characteristics [1]. In the special case when HiPIMS

Tuesday Morning, October 23, 2018

pulses have similar pulse shapes $I(t)$ at various voltages, one may reduce the description to *peak* current - voltage characteristics and arrive again at a power law $I_p = K V^n$, this time with n in the range between 1 and 2. Most interesting, however, is the case when the $I(t)$ curves are more complicated because they contain additional information. Since the appearance of publication [1] more than a decade ago we have learned a lot about HiPIMS, such as the relative importance of self-sputtering and gas recycling [2], leading to a more unified model [3]. In this contribution, I - V - t characteristics are revisited in light of today's knowledge.

Acknowledgments: The experimental data for this work were primarily generated during the tenure of the author at Lawrence Berkeley National Laboratory, Berkeley, California.

[1] A. Anders, J. Andersson, A. Ehasarian, J. Appl. Phys. 102 (2007) 113303.

[2] A. Anders, J. Čapek, M. Hála, L. Martinu, J. Phys. D: Appl. Phys. 45 (2012) 012003.

[3] N. Brenning, J.T. Gudmundsson, M.A. Raadu, T.J. Petty, T. Minea, D. Lundin, Plasma Sources Sci. Technol. 26 (2017) 125003.

12:00pm **SE+PS-TuM13 Advantages Associated with Applying a Positive Pulse Option to a HIPIMS Power Supply, Jason Hrebik**, Kurt J. Lesker Company

HIPIMS is an ionized PVC technique that produces a high density, high performance films. The extreme power densities in HIPIMS create a higher ionized plasma that creates a very high energy of material being deposited onto the substrate.

Many advanced techniques have been found to further enhance the quality of HIPIMS films, creating more ideal process and applications for utilizing this technique.

We will show advantages of integrating a positive "kick" pulse into a HIPIMS application. The "kick" pulse is an ideal feature for reactive sputtering applications due to its ability to carry out the HIPIMS plasma for extended period of time, minimizing the disappearing anode effect and repelling metal ions from the plasma toward the substrate resulting in higher sputtering rates.

Plasma Science and Technology Division Room 104C - Session PS+PB+SE-TuA

Atmospheric Pressure Plasmas

Moderators: Francois Reniers, Université Libre de Bruxelles, Steven Vitale, MIT Lincoln Laboratory

2:20pm PS+PB+SE-TuA1 Compact, Low Cost Atmospheric Pressure Plasma Jets Driven by Piezoelectric Transformers, Michael Johnson, National Research Council; *D.R. Boris, L. Petrova, S.G. Walton,* Naval Research Laboratory

In order for non-thermal atmospheric pressure plasma technology to be used for applications outside of the laboratory, there is a need to develop low-cost, portable devices that can be used for applications in the field. Constructing portable power supplies that can produce stable, non-thermal plasmas in full density air can be challenging as large electric fields are required to generate breakdown. Piezoelectric transformers are solid state transformers that can produce large gains in voltage, which makes them attractive candidates for plasma production. In this work, a piezoelectric transformer is used to amplify a low voltage AC signal in order to produce an atmospheric pressure plasma jet. Using this approach, plasma jets were generated with input voltages as low as 10 V when the piezoelectric transformer was operated at its resonance frequency (≈ 88 kHz). The electrical and optical characteristics of the piezoelectric driven plasma jet was compared to a plasma jet produced using a conventional high voltage sine wave of comparable operating frequency. Both jets were examined in helium and argon for a variety of different flow rates and operating voltages. The length of the jets were measured to determine if the piezoelectric transformer limited the potential size of the plasma jet. The current carried by the plasma jets were measured along with optical emission spectroscopy to examine the relative characteristics of the jets. Together, the results suggest the piezoelectric material may have influence beyond simple voltage amplification.

This work was supported by the Naval Research Laboratory Base Program. This research was performed while Michael Johnson held an NRC Research Associateship award at the U.S. Naval Research Laboratory.

2:40pm PS+PB+SE-TuA2 Process Regimes of Atmospheric Pressure Plasma-enhanced Chemical Vapor Deposition with Source Materials Highly Diluted in Inert Gases, SeungJae Baik, J. Jang, Hankyong National University, Republic of Korea; *H.-J. Oh,* Yonsei University, Republic of Korea Plasma-enhanced chemical vapor deposition (CVD) is appropriate for fast deposition with moderate film quality, but to form high quality materials such as epitaxial thin films, thermal processes at higher temperature are more favorable. High energy particles that are statistically produced in plasma processes are sources of film quality degradation. It has been previously reported that the plasma process at high working pressure, e.g., atmospheric pressure is feasible for epitaxial Si growth; where source gas species are highly diluted in inert gas. Employing a large dilution of source materials opens a new process regime in plasma-enhanced CVD: (1) low damage plasma processing (2) high deposition rate process with controlled powder generation (3) efficient usage of source materials.

We have performed Si thin film deposition processes with silane and hydrogen as source materials highly diluted in He or Ar gases under working pressure close to the atmospheric pressure (up to 700 torr). The new process regimes showing low damage plasma processing, high deposition rate with controlled powder generation, and efficient usage of source materials are experimentally demonstrated in various process conditions. In addition, the impurity incorporation into the film during deposition processes degrades the crystalline quality of the deposited Si thin films, which can be improved by employing plasma electrode pre-coating or pre-deposition cleaning process. Furthermore, the trade-off relation of plasma power and gas flow velocity revealed the process window of polycrystalline thin film deposition, and even epitaxial growth.

Atmospheric plasma-enhanced CVD tool is promising for fast deposition and low damage processing, and moreover, cheaper setup may also be viable via pre-deposition cleaning processes instead of utilizing expensive vacuum facilities.

3:00pm PS+PB+SE-TuA3 Plasma-enhanced Chemical Film Conversion (PECFC): Direct, Low-temperature Growth of Solution-processible and Printable Layered Thin Films, T. Liu, R. Mohan Sankaran, Case Western Reserve University

In plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD), the addition of a plasma to dissociate or excite the gas molecules and create active chemical and energetic species can lower the thermal energy required at the substrate to drive thin film nucleation and growth. Here, we show that a similar approach can be used to lower the temperature required to convert molecular precursors deposited from solution onto a substrate to a functional, crystalline thin film which we term plasma-enhanced chemical film conversion (PECFC). We apply this method to layered materials such as hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) whose applications are currently limited by the lack of large-area, low-temperature, direct (substrate independent) growth processes.

Our experimental setup consists of an atmospheric-pressure, planar, dielectric barrier discharge and a cold wall substrate heater. Single molecular precursors for h-BN, ammonia borane, or MoS_2 , ammonia tetrathiomolybdate were dissolved in solution and deposited by a variety of methods including dropcasting, airbrush spraying, spin coating, and inkjet printing on different substrates such as silicon (Si), silicon dioxide (SiO_2), and copper. The area of the film was only limited by the current size of our plasma source which is ~ 2 in². After conversion, the films were characterized by X-ray diffraction, micro Raman spectroscopy, atomic force microscopy, scanning electron microscopy, and transmission electron microscopy. We systematically compared thermal and plasma-assisted conversion at the same temperatures, background gas environments, and substrates. For h-BN, our results show that thermal conversion requires a minimum of 800 °C to nucleate on SiO_2 , but only 650 °C with the addition of a plasma. Adding 20% H_2 enables a further 150 °C reduction for plasma conversion. For MoS_2 , our results show that nucleation is enhanced in the presence of a plasma at the same growth temperature of 500 °C and a subsequent annealing step leads to a smooth (<0.2 nm RMS surface roughness) and highly crystalline film. We suggest that plasma species, especially atomic hydrogen (H), are involved in several important surface reaction mechanisms including abstraction of hydrogen, insertion in strained bonds, and radical formation, to enhance grain growth that overall enhance nucleation and growth of crystalline domains. We will also discuss the performance of the PECFC materials in electronic and energy devices.

3:20pm PS+PB+SE-TuA4 Plasma-based Remediation of Nanoscale Particulate Matter in Charbroiler Smoke Emissions, Sisi Yang, S. Subramanian, University of Southern California, Los Angeles; *D. Singleton,* Transient Plasma Systems; *C. Schroeder, W. Schroeder, M. Gundersen, S.B. Cronin,* University of Southern California, Los Angeles

Recent studies have shown ultrafine particulate matter (UFP) produced in commercial charbroiling processes represents a serious health hazard and has been linked to various forms of cancer. In this study, we demonstrate a highly effective method for treating restaurant smoke emissions using a transient pulsed plasma reactor based on a nanosecond high voltage pulse generator. We measure the size and relative mass distribution of particulate matter produced in commercial charbroiling processes (e.g., cooking of hamburger meat) both with and without the plasma treatment. Here, the plasma discharge is produced in a 3" diameter cylindrical reactor with a 5-10 nanosecond high voltage (17 kV) pulse generator. The distribution of untreated nanoparticle sizes peaked around 125-150 nm in diameter, as measured using a scanning mobility particle sizer (SMPS) spectrometer. With plasma treatment, we observe up to a 55-fold reduction in total particle mass and a significant reduction in the nanoparticle size distribution using this method. The effectiveness of the UFP remediation increases with both the pulse repetition rate and pulse voltage, demonstrating the scalability of this approach for treating higher flow rates and larger systems.

4:20pm PS+PB+SE-TuA7 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: In situ Measurements of Electron Heating in Materials, Scott Walton, U.S. Naval Research Laboratory; *J. Tomko, B.M. Foley,* University of Virginia; *D.R. Boris,* U.S. Naval Research Laboratory; *M.J. Johnson,* National Research Council; *Tz.B. Petrova,* U.S. Naval Research Laboratory; *A. Giri, P.E. Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest since both contribute to the physicochemical changes during plasma-based materials processing. A unique feature of plasmas compared to other methods of materials

Tuesday Afternoon, October 23, 2018

synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the electrons propagate radially from the point of contact. These results, in conjunction with voltage and current measurements, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet-surface interactions. This work is partially supported by the Naval Research Laboratory base program.

4:40pm PS+PB+SE-TuA8 Surface Activation by Atmospheric Plasma: the Right Technology for the Right Application, A. Ozkan, D. Merche, Francois Reniers, Université Libre de Bruxelles, Belgium

Cold atmospheric plasma are widely used for surface activation in many applications. Today, many technologies are available, such as coronas, dielectric barrier discharges (DBDs), remote (or post-discharge) DBDs, torches, operating in the radiofrequency mode, gliding arcs, A wide variety of operating conditions can be found in the literature or on the websites of the manufacturers : AC, DC, kHz range, noble gas or air, high or low power, For the scientist, the lab manager, or the CTO of a company looking for a new, clean, activation technique, the vast list of possibilities, although representing opportunities, may represent a challenge. In this paper, we try to set up a product driven roadmap to help the scientist making the best choice for the plasma technology to implement for his application. Through a few selected examples, all tested in our laboratory equipped with 7 different plasma technologies and 15 reactors, we show which is the best technology for the application of interest. Advantages and drawbacks of each of the tested technologies with respect of the material, the energy consumption, and the time and cost of operation are presented, and discussed in terms of plasma and surface characterization.

The applications chosen addresses a wide range of questions such as:

- which plasma to chose to clean and activate glass substrates (a comparison between torches and in-situ DBDs is proposed)
- atmospheric plasma to grow an oxide layer on aluminium : a comparison between an air operated torch and plasma electrolytic oxidation
- how to activate a macroscopic 3D pre-painted metal piece for further painting using an atmospheric plasma torch. A comparison between 4 torches is presented
- how to activate the surface of selected polymers using DBD, RF torches with different gases
- how to activate surfaces (silicon, polymers, nanotubes) for further grafting of metal nanoparticles
- how to modify PTFE using a torch, what are the side effects, and why.

These examples will be starting points for a more general discussion about methodology, based on the final expectations and the chemistry and physics of each technology.

5:00pm PS+PB+SE-TuA9 Aluminum Alloy Surface Cleaning by Atmospheric Pressure Microwave Discharge, Lucia Bonova, W. Zhu, A. Farrokhanah, D.V. Krogstad, Z.K. Jeckell, S. Chaudhuri, D.N. Ruzic, University of Illinois at Urbana-Champaign

Aluminum and its alloys are commonly used as lightweight materials in many industrial sectors including aerospace. During the manufacturing process of aluminum, a series of lubricants and additives are used to avoid sticking of layers and prevent degradation or corrosion. The residual hydrocarbon film is typically removed by a chemical chromate process prior to the deposition of an anticorrosive layer. We present an alternate method to remove the hydrocarbons deposited on the aluminum surface by an atmospheric pressure microwave discharge.

The Center for Plasma Material Interaction (CPMI) at University of Illinois has developed novel patented technologies of Evaporative Coatings at Atmosphere Pressure (ECAP) using a 2.45 GHz microwave power to treat the aluminum surface with an air plasma at atmospheric pressure. The

cleaning effect of this microwave plasma was analyzed by contact angle measurements, XPS and ATR-FTIR.

5:20pm PS+PB+SE-TuA10 Temporal and Spatial Study of a Parallel pin-plate Plasma Reactor, Vladimir Milosavljević, M. Gulan, L. Scally, P.J. Cullen, BioPlasma Research Group, Dublin Institute of Technology, Dublin, Ireland

Electrical discharges in gases have demonstrated a wide range of effects for material science and energy applications. Under both laboratory and industrial setups, such electrical discharges can produce a stable plasma. From both fundamental and applied purposes, such gaseous plasmas are well studied, the technology has found many applications. Recent interest has turned to operating such plasma under atmospheric conditions. The main advantage of the plasma discharge at atmospheric pressure over low-pressure plasma or high-pressure plasma, is that no reaction vessel is needed. However, with increasing gas pressures, the stability and reproducibility of the plasma discharge are significantly impacted. For atmospheric pressure, in order to obtain a stable plasma discharge in addition to the electrodes a dielectric barrier is required. The function of this dielectric is to spread the electrical charge throughout the entire electrode in order to create multiple conducting paths for the discharges to occur. This is the foundation of the Dielectric-barrier discharge (DBD). One or both electrodes in DBD could be covered by a dielectric material which serves as an electric polarizer, and helps maintain a low gas temperature. Over the course of its life, for any DBD system, the biggest disadvantage is the dielectric contamination. In most cases, this dielectric is a polymer, and polymers are generally fragile materials. Therefore, developing a plasma system that does not require a dielectric, and has a reproducible and stable electrical discharge at atmospheric pressure would offer new system designs and applications.

This work presents a pulsing plasma system (PPS) which can run at atmospheric pressure under various external parameters. The system has a planar configuration with a bottom (grounded) flat electrode and a top multiple pin electrode (high voltage). The design of this PPS allows several parameters to be modified, such as: discharge frequency (30-125 kHz), duty cycle (1-100%), duty cycle frequency (100-3000 Hz), peak-to-peak voltage (up to 60 kV), power (up to 700 W), distance between electrodes (up to 55mm), and treatment time (unlimited). The new plasma system allows an increase in the surface-plasma interaction selectivity and to reduce plasma induced damages to surfaces. The electron properties and gas radical density generated for the system under such control parameters are reported.

This work was funded by the Dublin Institute of Technology and PlasmaLeap Technologies, Ireland.

5:40pm PS+PB+SE-TuA11 Plasma-modulated Metamaterials and Photonic Crystals, Jeffrey Hopwood, H. Kim, Tufts University

Metamaterials are periodic assemblies of man-made structures that can mimic naturally occurring materials. By clever design, electromagnetic transmission through metamaterials may have extraordinary properties such as negative refractive index. In this paper we describe the formation of atmospheric pressure argon microplasmas within metamaterials as well as photonic crystals. Microplasma ignition within these materials is initiated by first creating an implicit microwave or millimeter wave resonance within the structure. For example, a vacancy in the artificial crystalline structure can act as a millimeter wave cavity. Incident EM waves excite this resonance and the strong resonant electric field causes gas breakdown.

In general, metamaterials are pre-configured during the design process and exhibit fixed transmission characteristics. The self-initiated plasma, however, dynamically changes the metamaterial. We show that depending on the gas pressure and electron density, microplasma inclusions may act as dielectrics or conductors. Experimentally one observes that the appearance of microplasma causes a change in the material from transparent to reflective, or vice versa. A metamaterial consisting of an array of copper split-ring resonators (3x3x9) is described in terms of the plasma density and its microwave transmission from 1-3 GHz. The appearance of microplasmas quenches the resonance and decouples the resonators from one another; the transmission spectra are radically changed upon de-coupling. In the millimeter wave band, a photonic crystal consisting of alumina rods is shown to support argon plasma at 43 GHz. The transient response of the photonic crystal during pulsed EM radiation and plasma formation is measured and found to act as a power limiting device.

Tuesday Afternoon, October 23, 2018

6:00pm **PS+PB+SE-TuA12 Generation of Large-Volume Transient Glow Discharge Plasma by an External Fast Ionization Wave (FIW) from a Plasma Jet**, *Hamid Razavi, M. Laroussi*, Old Dominion University

A non-thermal transient glow discharge can be generated remotely in a nonconductive low-pressure chamber by an external guided fast ionization wave (FIW). We used an atmospheric-pressure LTP jet (APLTPJ) as an external source of FIW to transfer the enhanced electric field at the wavefront to a reduced-pressure Pyrex glass chamber with no electrical connection to the chamber [1]. Here, we study on the interaction of FIW with a dielectric surface which forms the wall of the low-pressure system.

In this study, key characteristics of the transient diffuse plasma are discussed. Plasma parameters were measured by Langmuir probe and APLTPJ electrical measurements were done to elucidate the operational mechanisms of the FIW as an igniter of a reduced pressure glow discharge plasma. It is shown that the transient discharge in the low-pressure chamber generates a bulk plasma with negative potential due to the nonconductive boundary. We also used Optical emission spectroscopy (OES) to show the physical and chemical characteristics of the APLTPJ plasma and the transient glow discharge plasma. It is shown that the glow discharge plasma is capable of producing second and third ionized nitrogen and oxygen atoms (OII, NII, and NIII). Fast images were taken by an intensified CCD to study the launching and propagation phases of both APLTPJ plasma and the transient reduced pressure glow discharge plasma as well as the incidence of the guided FIW on a dielectric surface.

[1] M. Laroussi and H. Razavi, "Indirect Generation of a Large Volume Diffuse Plasma By an Ionization Wave from a Plasma Jet", *IEEE Trans. Plasma Sci.*, Vol. 43, No. 7, pp. 2226-2229, (2015).

Advanced Surface Engineering Division Room 202C - Session SE-TuA

Wear, Oxidation and Corrosion Protective Coatings

Moderators: Suneel Kodambaka, University of California, Los Angeles, Andrey Voevodin, University of North Texas, Pantcho Stoyanov, Pratt & Whitney

2:20pm **SE-TuA1 Dissociative Extraction of Carbon-based Tribofilms from Hydrocarbon Molecules on Catalytically Active Nanocomposite Coatings**, *Ali Erdemir, G. Ramirez, O.L. Eryilmaz*, Argonne National Laboratory
INVITED

Diamondlike carbon (DLC) coatings are now used in large volumes to mitigate friction and wear-related problems in a wide range of moving mechanical assemblies [1]. In our laboratory, we have developed a class of new catalytically active nanocomposite coatings that can extract DLC type boundary films directly from the hydrocarbon molecules of lubricating oils and gas molecules and thus provide superior friction and wear properties. Specifically, these composite coatings are composed of catalytically active hard and soft nanophases affording exceptional catalytic responsiveness to the hydrocarbon molecules trapped at the sliding contact interface. When tested under lubricated sliding conditions, these coatings can crack or fragment hydrocarbon molecules and then deposit them on sliding surfaces as lubricious and highly protective boundary films. Using TEM, UV Raman and TOF-SIMS, we elucidated the structural chemistry of these boundary films and confirmed that they were indeed similar to conventional DLC films that are currently deposited using plasma-based CVD and PVD processes. TEM also confirmed the presence of graphene and carbon-nano-onions scattered within the tribofilm. Under severe sliding, reciprocating, and scuffing test conditions, these carbon-based boundary films showed extreme resistance to wear and scuffing [2].

[1] S-C. Cha and A. Erdemir, eds., "Coating Technology for Vehicle Applications" Springer, New York, 2015.

[2] A. Erdemir et al., *Nature*, 536(2016)67-71

3:00pm **SE-TuA3 Use of Carbon Nanotube-Silver Metal Matrix Composite Thin Films to Enhance Mechanical Properties of Grid Fingers and Busbars on Photovoltaic Cells**, *Cayla Nelson*, University of New Mexico; *O.K. Abudayyeh*, Osazda Energy, LLC; *Y. Shen, S.M. Han*, University of New Mexico

The hot spots created by cell cracks have recently been identified as the most common degradation mode in PV modules.¹ Even before they become hot spots, these cracks lead to high series resistance, reduced efficiency, and lost energy. To reduce this degradation, we have been investigating the use of multiwalled carbon nanotubes (MW-CNTs) as a

reinforcement in metal matrix composites. We have demonstrated that these composites provide gap-bridging capability (> 40 mm), "self-healing," and fracture toughness against the cracks forming in the substrate and the metal contacts.²⁻⁴ To accompany the experimental effort, finite element modeling (FEM) is used to relate the microstructure of the composite to its mechanical properties. The FEM models are compared to mechanical data taken by dynamic mechanical analysis (DMA). The composites are fabricated in a Ag/CNT/Ag layer-by-layer structure. The silver layer can be evaporated or electroplated, and the CNTs are spray-coated. The shape of the composite films is a dog bone structure that can be released from the substrate as a free-standing film. This release is necessary to extract the mechanical properties solely belonging to the composite. Fitting the FEM model to DMA measurements captures qualitative trends of how mechanical properties of the MMC change with CNT volume fraction. Combining mechanical modeling with experimental results provides predictive evaluation of CNT reinforced metal matrix composites.

¹ D. C. Jordan, T. J. Silverman, J. H. Wohlgemuth, S. R. Kurtz, and K. T. VanSant, "Photovoltaic failure and degradation modes," *Prog. Photovolt: Res. Appl.* **25**, 318-326 (2017).

² O. Abudayyeh, N. D. Gapp, D. M. Wilt, and S. M. Han, "Methods to Mitigate Stress-Induced Metal Line Fractures for Thin-Film Solar Cells, Using Metal-Carbon-Nanotube Composites," Patent No. Application No. PCT/US2016/038197 (2016).

³ O. K. Abudayyeh, G. K. Bradshaw, S. Whipple, D. M. Wilt, and S. M. Han, "Crack-Tolerant Metal Composites as Photovoltaic Gridlines," *Appl. Phys. Lett.*, submitted (2018).

⁴ O. K. Abudayyeh, N. D. Gapp, C. Nelson, D. M. Wilt, and S. M. Han, "Silver-Carbon-Nanotube Metal Matrix Composites for Metal Contacts on Space Photovoltaics," *IEEE J. Photovolt.* **6**, 337-342 (2016).

3:20pm **SE-TuA4 Study of Effects of Synergistic Environmental Exposures on Fiber-Reinforced Polymer Composites Protected by Metallic Coatings**, *Arash Afshar, D. Mihut, S. Hill*, Mercer University School of Engineering

Polymer composites are good candidates for applications requiring high strength, low weight and corrosion resistance properties. Therefore, they are widely being used in marine, automotive, construction, aerospace industries to name a few. However, the main existing challenge is preventing the degradation of composite materials under prolonged exposure to harsh environmental conditions such as UV radiation and moisture. Composite samples with standardized sizes were exposed to combined UV radiation and moisture in the environmental chamber for different time intervals. Some samples were coated with optically thick metallic materials using high vacuum magnetron sputtering deposition and were later exposed to the same combined environmental conditions. It was observed that metallic coatings improved the surface resistance of the substrate composite materials and protected the mechanical properties throughout the course of exposure. The surface morphology of samples before and after exposure was observed using optical microscopy and the adhesion of metallic layers to the substrates was examined using scanning electron microscopy. The mechanical properties were also characterized using flexural and hardness tests over the exposure time.

4:20pm **SE-TuA7 Atomistic View of Mg Metal Corrosion Using *in-situ* cryo-XPS and *ab initio* Computation**, *Vaithiyalingam Shutthanandan, A. Martinez, P.V. Sushko, A. Devaraj, E. Stevens, O.A. Marina, V. Joshi, S. Thevuthasan, V. Murugesan*, Pacific Northwest National Laboratory

Magnesium metal is potential candidate for high strength to weight ratio alloys with wide application in aerospace and automotive industries. However, poor corrosion resistance under ambient environmental conditions is the bottleneck for industrial deployment. Designing passivation layers and/or corrosion resistance alloys require fundamental understanding of the corrosion process. The traditional *ex-situ* spectroscopic measurements of polycrystalline metal surface with ubiquitous surface impurities provided indistinct view of the corrosion process. To clearly distinguish the mechanism and sequence of corrosion process, we employed *in-situ* cryo-based x-ray photoelectron spectroscopy (XPS) measurements on well-defined Mg-single crystal surfaces in combination with *ab initio* atomistic modelling studies. Mg (0001) surfaces were exposed to ambient water conditions (i.e. D₂O and 5 wt% NaCl+95 wt% D₂O solution) and the subsequent interfacial reactions were studied through integrated experimental and theoretical approach. This study provides atomistic view of Mg(OH)₂ nucleation as main product of the corrosion process. Under salt conditions, the competitive nucleation process between Mg(OH)₂ and MgCl₂ were observed. High resolution helium ion microscopy images of the corroded surface show unique

Tuesday Afternoon, October 23, 2018

morphologies of nucleates including some well-defined faceted cubic crystals and micron size faceted ribbon like structures. By combining the energy requirements from computational modelling and the electronic states of corrosion products, the mechanism and sequence of the corrosion process on Mg metal will be discussed.

4:40pm SE-TuA8 Scratch Behavior and Modelling of Cu/Si(100) Thin Films Deposited by Modulated Pulsed Power Magnetron Sputtering, D. Meng, Y.G. Li, M.K. Lei, Dalian University of Technology, China

A series of copper films on Si(100) substrate were deposited using modulated pulsed power magnetron sputtering under different sputtering pressure from 0.11 to 0.70 Pa. The scratch behavior of copper films on Si(100) was evaluated by scratch adhesion test with the aid of finite element modelling. With the increase of pressure, the surface morphology becomes rougher and the pattern transforms from compact fine granular structure to coarse and crack visible columnar structure, and the surface morphology of scratch tracks transforms from no obvious delamination to vast delamination. At pressure of 0.11 Pa, no obvious delamination can be observed, while copper films begin to delaminate with the growing pressure at 0.3 Pa and above at a certain load. Critical loads L_{c1} to L_{c4} were employed to assess the adhesion behavior of soft copper films on hard Si(100), the main exhibiting characteristics were the periodical plastic deformation on the side of scratch tip and semi-circular characteristic behind the scratch tip which were mainly caused by plastic deformation in the stick-slip process. Finite element modeling was employed to analyze the stress and strain responses of scratch on copper films by mainly using the maximum principal stress σ_1 as a function of normal loads in stress concentration zone A, B and C. The location of the peak σ_1 migrates from zone B to C which are tensile as the normal load increases, while peak σ_1 in zone A is compressive. The directionality of σ_1 for zone B tilts mostly at an out-of-plane angle mostly about 15° and 90° which may be responsible for the interface failure between the film and substrate. Critical loads L_{c1} and L_{c2} are evaluated through the migration of peak σ_1 from zone B to C, while critical load L_{c3} is associated with stress accumulation in zone C and stress accumulation in zone A is responsible for critical load L_{c4} . The observed plastic deformation and failure modes are able to further illustrate the physical meaning of critical loads.

5:00pm SE-TuA9 Corrosion Resistance of Mechanically Reinforced Aluminium based Coatings obtained by PVD Techniques, Frederic Sanchette, UTT - Université de Technologie de Troyes, France; J. Creus, Université de La Rochelle, France; A. Billard, FEMTO-ST, France **INVITED** Aluminium-based alloy films can be used for the protection of steels against corrosion. However, the mechanical properties of such coatings must be reinforced, for example by addition of transition elements, which have low diffusivity and low solubility in aluminum. Various aluminium based alloys elaborated by Electron Beam Physical Vapour Deposition (EBPVD) or magnetron sputtering techniques are characterised in terms of mechanical properties and corrosion behaviour in saline solution. The incorporation of transition metals permits to modify the mechanical or physico-chemical characteristics of aluminium coatings, so several alloying elements are compared. Evolution of microstructure of the Al based coatings is discussed versus the alloying element content. Different compositions of alloys are examined.

This presentation summarizes the main results of studies conducted in this field since the early 1990s. This is a synthesis of the main tendencies reported during the evaluation of the mechanical and corrosion properties of these alloys.

The objective is to build a reactivity classification in saline solution of several Al based coatings synthesized by vacuum deposition techniques. Combined with the classification of mechanical properties, these standards would become relevant guides in the choice of PVD coatings and/or alloys for applications exposed to saline environments. In our study, this guide is helpful in the synthesis of nanometric multi-layer architectures, which proves to be a promising way to combine improved mechanical properties with sacrificial character for the future coating configurations.

5:40pm SE-TuA11 High Temperature Mechanical Properties of CrAlN and CrAlSiN Hard Coatings, Aljaž Drnovšek, M. Rebelo de Figueiredo, A. Xia, Montanuniversität Leoben, Austria; S. Kolozsvári, Plansee Composite Materials GmbH, Germany; H. Vo, P. Hosemann, University of California Berkeley; R. Franz, Montanuniversität Leoben, Austria

One of the most common methods used to characterize the mechanical properties of hard coating materials is nanoindentation. The further development of nanoindentation in recent years led to new ex-situ and in-

situ systems that are capable of measuring mechanical properties such as hardness, elastic modulus and fracture toughness at elevated temperatures. In addition, new measuring procedures such as nano-dynamic mechanical analysis (n-DMA) enable measuring the hardness and elastic modulus at a continuous rate through the entire penetration depth at reduced thermal drift sensibility. This approach yields faster measurements at high temperatures which is beneficial in terms of tip degradation and generally renders the obtained results more reliable. With these new experimental possibilities, the mechanical properties of hard coatings synthesized by physical vapor deposition techniques can now be characterized close to the service temperatures that can reach up to 1000 °C.

In the current work, we tested two magnetron sputtered coatings that are widely used in industrial cutting applications, namely CrAlN and CrAlSiN. The latter is a further development of CrAlN coatings where the columnar growth is interrupted due to the addition of Si resulting in a nanocomposite composed of crystalline CrAl(Si)N grains and an amorphous SiN_x grain boundary phase. In particular in the case of CrAlSiN hard coatings, studies analyzing the mechanical properties at high temperature are scarce. High temperature nanoindentation measurements on both coatings were performed up to 700 °C in steps of 100 °C. The room temperature hardness values of 30 GPa (CrAlN) and 36 GPa (CrAlSiN) reduced by approximately 2 GPa per temperature step up to 500 °C. Above this temperature, the hardness of CrAlN continued to decrease while the hardness of CrAlSiN remained largely unchanged. In addition, high temperature tribological tests were conducted in air and inert atmosphere in the same temperature range in order to link the friction and wear behavior to the obtained mechanical properties. This data set is intended to serve as a first step towards a more comprehensive understanding of the high temperature mechanical and tribological properties of hard coatings which is vital for their further development and improvement.

6:00pm SE-TuA12 Thick CrN/AlN Superlattice Coatings for Solid Particle Erosion and High Temperature Wear Resistant Applications, Jianliang Lin, Southwest Research Institute

Energetic ion bombardment is critical to improve the structure and properties of coatings in plasma assisted depositions. Plasma enhanced magnetron sputtering (PEMS) is an advanced version of conventional magnetron sputtering by generating a global plasma, in addition to the magnetron plasma, in the entire deposition system using hot filament thermionic emission to enhance the ionization and bombardment. In this study, thick CrN/AlN superlattice coatings (15 to 20 μm) were deposited by reactive sputtering using a combination of PEMS and high power impulse magnetron sputtering (HiPIMS) techniques. These coatings were deposited at different PEMS plasma discharge currents (0 to 4 A) which represent different ion fluxes for the bombardment. The bilayer thickness of the nanolayers was controlled in the range of 4 to 7 nm. The microstructure of the coatings gradually changes from long columnar grains to extremely dense structure with an increase in the PEMS discharge current. These coatings exhibited high hardness, excellent adhesion, and excellent resistance to high temperature wear, oxidation and solid particle erosion. The high temperature wear resistance of selected coatings was measured using a high temperature pin-on-disc tribometer in the ambient air from 600 °C to 1000 °C. The solid particle erosion resistance of these thick CrN/AlN coating was evaluated and compared with other thick hard coatings, e.g. CrN, TiN, TiSiCN, etc., using an air jet sand erosion tester. In this presentation, PEMS/HiPIMS deposition process, the coating microstructures, erosion, and high temperature wear test results will be discussed.

Advanced Surface Engineering Division Room Hall B - Session SE-TuP

Advanced Surface Engineering Division Poster Session

SE-TuP2 Fabrication of Porous Membranes of Controlled Porosity and Chemical Functionality, *Golnaz Dianat, M. Gupta, S. Seidel, M.M. Deluna*, University of Southern California

We present a modified initiated chemical vapor deposition (iCVD) technique to synthesize porous polymer membranes. We demonstrate that we can pattern the deposition of the porous polymer membranes by using poly(dimethylsiloxane) (PDMS) masks. The porosity and thickness of the membranes can be controlled by varying the substrate temperature during monomer deposition. The functionality of membrane can be tuned by addition of a cross-linker during polymerization and allow for the fabrication of robust free-standing shaped membranes. Our ability to control the shape, thickness, porosity, and functionality of the porous membranes allows for the design of new surfaces for a variety of applications in sensors, filtration, and microfluidics. Asymmetric polymer membranes, that are composed of a dense top layer and porous bottom layer, can be synthesized using a combination of conventional and nonconventional iCVD conditions in a one-pot process. This method allows for a high degree of control over the thickness of the dense layer by simply controlling the deposition time and paves the way to synthesize ultrathin dense layers with sub-50nm thickness that is difficult to attain using other methods. The functionality of the dense and porous layers can be independently tailored to be either hydrophobic or hydrophilic, resulting in membranes that are fully hydrophilic, fully hydrophobic, or asymmetric in both structure and chemical functionality.

SE-TuP3 Plasma Treatment of Thiol-Carborane Self-Assembled Monolayers on Copper, *Michelle Paquette, R. Thapa, L. Dorsett, S. Malik, S. Wagner, A.N. Caruso*, University of Missouri-Kansas City; *D. Merrill, J.D. Bielefeld, S.W. King*, Intel Corporation

Thiol-carborane self-assembled monolayers (SAMs) have been used to modify the properties of metal surfaces. Not only do the symmetric twelve-vertex icosahedral carborane molecules provide a unique and appealing geometry for SAM formation, but boron carbide materials are notorious for their chemical, thermal, and mechanical robustness. Carborane-based SAMs have been shown to provide superior corrosion resistance on silver as well as the ability to modify the electronic properties (e.g., work function) of gold and silver surfaces. One of the noteworthy properties of carboranes is their ability to cross-link via labile hydrogen bonds under the influence of heat, plasma, and various energetic particles. Here, we investigate the influence of various plasma treatments on carborane monolayers on copper and show how these can be used to both further tune their properties as well as influence their stability.

SE-TuP4 Improved Light Extraction Efficiency using Homeotropic Thin Films on SiO₂ Micro Pillars, *J.H. Lee, Y. Lin, G. Wu*, Chang Gung University, Taiwan

It has been known that high refractive index material such as gallium nitride film has been limited for light extraction by low total internal reflection angle. The external quantum efficiency for a light-emitting diode is thus low due to absorption by the semiconductor material and the substrate. In this paper, we proposed to use homeotropic, vertical alignment, liquid crystal polymer coatings on patterned SiO₂ micro - pillar arrays to improve the light extraction of nitride light-emitting diodes. A wet etching technique was firstly employed to create the patterned SiO₂ micro-pillar arrays on the surface. The pillar was nominally 3 μm in diameter, 200-600 nm in height, and the period was 6 μm for a triangular array. Then we coated 5 wt% liquid crystal polymer precursor uniformly on the surface of the etched structure. The results showed that the homeotropic optical thin-film improved light guiding, and the light escape cone angle increased from 26 to 50-60 degrees by the viewing angle test system at an injection current of 20 mA. The light extraction efficiency was also increased by 59% by using an integrating sphere.

Keywords: Liquid crystal polymer, Light-emitting diode, SiO₂ micro - pillar

This work was supported in part by the Ministry of Science and Technology under research grants MOST105-2221-E182-059-MY3 and CMRPD2E0481.

SE-TuP5 Investigating the Influence of Substrate Cleaning on the Solution Stability of Plasma Polymer Films, *Karyn Jarvis*, Swinburne University of Technology, Australia; *S.L. McArthur*, Swinburne University of Technology and CSIRO, Australia

Plasma polymerization modifies surfaces via the deposition of a thin film possessing specific functional groups. The organic monomer is introduced into the low pressure chamber as a vapour, fragmented via radio frequency and deposited onto all surfaces in contact with the plasma. Commonly used monomers such as octadiene, allylamine and acrylic acid enable the deposition of hydrocarbon, amine and carboxylic acid terminated surfaces respectively. Surface cleaning prior to the deposition of thin films is frequently carried out to improve film adhesion. The use of plasma polymer films in biomedical applications has increased the demand for coatings suitable for use in physiological conditions. Significant changes in film properties in aqueous conditions have serious implications on the incorporation of these films in biomedical technologies and devices.

In this study, silicon wafer substrates were cleaned by several different methods prior to the deposition of plasma polymerized thin films to investigate the influence of substrate cleaning on film stability in aqueous solutions. The substrates were used untreated or cleaned by liquid sonication, UV/ozone cleaning or air plasma. X-ray photoelectron spectroscopy (XPS) and contact angle measurements were undertaken to determine the effect of the cleaning method on surface chemistry and wettability. After cleaning, the substrates were coated by plasma polymerized octadiene, acrylic acid or allylamine thin films. The surface chemistries and film thicknesses of the plasma polymerised films were determined by XPS and variable angle spectroscopy ellipsometry respectively. The plasma polymerised films were immersed in both Milli-Q water and phosphate buffered saline for time periods of 1, 24 and 168 hours. Films were again analysed via XPS and ellipsometry to determine the influence of substrate cleaning, immersion solution and immersion duration on film stability. Substrate cleaning was shown to have an influence on film stability with visible pitting on some films, even after only 1 hour of immersion. Substrate cleaning is an important step prior to the deposition of thin films and can be used to extend the solution stability of plasma polymerised films, which has important implications for a variety of biomedical applications.

SE-TuP6 Tribological Systems Solutions for Gas Turbine Engines, *Pantcho Stoyanov*, Pratt & Whitney

The advancement of durable gas turbine engine components depends heavily on the development of high-performance materials, which can withstand extreme environmental and contact conditions (e.g. large temperature ranges, high contact pressures, and continuous bombardment of abrasive particles, all of which degrade the physical properties). In particular, due to the large number of complex contacting and moving mechanical assemblies in the engine, the lifetime of certain structures is limited by the tribological performance of the employed materials and coatings. This talk will provide an overview of tribological solutions employed in several sections of gas turbine engines. After a general review of aircraft engine tribology, the talk will focus on coatings used for clearance control (i.e. abradable air seals) as well as tribological materials used to minimize fretting type of wear. More specifically, a study will be presented on the influence of self-lubricating hexagonal boron nitride (hBN) on the erosion and abrasability of Ni-based abradable coatings. Subsequently, a series of studies on the friction and wear behavior of Ni-based and Co-based superalloys at elevated temperatures will be presented. Emphasis will be placed on the correlation between the third body formation process (e.g. oxide layer formation, transferfilms) and the tribological behavior of the superalloys. This talk will conclude with the future strategies of tribological coating solutions in Pratt & Whitney's PurePower® PW1000G family of engines.

SE-TuP7 Effect of Laser Processing on the Atmospheric Corrosion Behavior of Mg Alloy AZ31B and Weldments, *M.A. Melia*, Sandia National Laboratories; *L. Agnew, J.M. Skelton, J.R. Scully, James Fitz-Gerald*, University of Virginia

The widespread implementation of lightweight magnesium alloys to the automotive and aerospace industries is currently limited by its poor and unpredictable corrosion response. Of major concern is the localized corrosion of Mg alloys, driven by a uniform population of electrochemically noble secondary phases present in the chemically heterogeneous microstructure, resulting in a rapid loss of structural integrity. These microstructural heterogeneities are accentuated when Mg alloys are welded causing galvanic coupling between weld zones. A research

Tuesday Evening Poster Sessions, October 23, 2018

investigation to mitigate localized corrosion of a Mg alloy (AZ31B), with and without weldments, via laser surface engineering has been conducted.

Lasers operating in a nanosecond pulse duration regime are capable of melting and solidification rates on the order of 10^9 K/s with the ability to extend the solid solubility limit of the alloying elements. The irradiation of AZ31B with an excimer laser (FWHM= 25ns, λ = 248nm) observed significant changes in the near surface microstructure and secondary phase particle dissolution, characterized in this case by scanning electron microscopy equipped with a backscatter electron detector. The corrosion response of

Mg alloy AZ31B (3wt% Al, 1wt% Zn, 0.6wt% Mn, and Mg balance) was investigated using the accelerated atmospheric test (GMW14872) for 30 wet-dry cycles. The atmospheric exposure test consists of a 24-hour cycle involving three 8-hour stages. During the first stage, samples are held at ambient temperature and humidity (25 °C, 45% RH) and are sprayed every 90 minutes with a salt solution (0.9% NaCl, 0.1% CaCl₂, 0.075% NaHCO₃).

During the second stage the temperature is increased to 49 °C and samples are continuously sprayed with a deionized water fog (~100% RH). During the third stage temperature is increased to 60 °C and held at less than 30%

relative humidity. The corrosion product was analyzed using Fourier transform infrared spectroscopy (FTIR) and grazing incident x-ray diffraction (GI-XRD). At early stages of the exposure experiments the laser processed specimens showed less corrosion product coverage than as-polished or welded specimens.

Nanometer-scale Science and Technology Division Room 203A - Session NS+2D+AN+MN+MP+SE-WeM

Micro, Nano and Opto Mechanics

Moderators: Robert Ilic, National Institute of Standards and Technology, Alokik Kanwal, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+MN+MP+SE-WeM2 The Collective Behavior of Large Ensembles of Coupled MEMS Cantilevers with Varying Natural Frequencies**, *Christopher Wallin*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *N. Dick*, Tel Aviv University, Israel; *R. De Alba, D.A. Westly*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *S. Grutzik*, Sandia National Laboratories; *A.T. Zehnder, R.H. Rand*, Cornell University; *V.A. Aksyuk*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *S. Krylov*, Tel Aviv University, Israel; *B.R. Ilic*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology

The collective behavior of nonlinear, coupled micro- and nano-electromechanical (M/NEMS) resonators has been shown to exhibit a host of nontrivial dynamics including abrupt pattern switching, multistability, hysteresis, intrinsically localized modes, and synchronization. Additionally, M/NEMS resonator arrays are extremely responsive to environmental perturbations making them excellent candidates for sensing applications when operated linearly. With our work, we investigate the collective dynamics of coplanar interdigitated arrays of prismatic microcantilevers operating in both the nonlinear and linear regimes.

Two opposing, partially interdigitated cantilever arrays with 100 cantilevers apiece were fabricated using a silicon-on-insulator wafer. The device consists of a unique geometry in which each array has cantilever lengths expanding linearly across the device in opposite directions giving a distribution of natural frequencies. The arrays were engineered to allow for large scale, nonlinear out-of-plane beam deflections through the removal of the entire silicon handle layer beneath the active array area.

For sufficiently large drive amplitudes, the resonators begin oscillating via combination parametric resonance (CPR) across the entire array. The CPR driven oscillations occur across a broad frequency band. The tunable coupling between nearest-neighbor cantilevers through fringing electrostatic fields provides a mechanism to vary the CPR response. Due to the sizable deflections, the device's nonlinearities are apparent including hysteresis effects. Our experimental results are supported and expanded by the development of a reduced order model based on the Galerkin decomposition which generates the leading features of our data including the CPR band.

When operating in the linear regime, the natural modes of the array have localized characteristics whereby a limited number of beams oscillate at each of the natural mode frequencies. Operating the device at higher harmonics increases mode separation as the propagation bands stretch. The distinct resonant peak separation coupled with the spatially confined modal response make higher harmonic operation of tailored, variable length cantilever arrays well suited for a variety of resonant based sensing applications.

8:40am **NS+2D+AN+MN+MP+SE-WeM3 Piezoelectric Optomechanical Systems**, *Krishna Coimbatore Balram*, University of Bristol, UK **INVITED**
Nanoscale optomechanical systems, which rely on the strong interactions between co-localised optical and mechanical modes in nanoscale cavities, have been explored for a wide variety of applications ranging from sensing to signal transduction [Aspelmeyer et al., Rev. Mod. Phys. (2014)]. In this talk, I will discuss piezoelectric optomechanical platforms for efficient signal transduction between the radio frequency (RF) and optical domain. We use GaAs as our model platform (Balram et al., Optica (2014), Nature Photonics (2016), Phys. Rev. Applied (2017)) and discuss some of the research opportunities and challenges in this field, especially as we move towards higher mechanical frequencies (> 10 GHz).

9:20am **NS+2D+AN+MN+MP+SE-WeM5 Absolute Deflection Measurements in a MEMS/NEMS Fabry-Perot Interferometry System**, *Roberto De Alba, C.B. Wallin, G. Holland*, National Institute of Standards and Technology; *S. Krylov*, Tel Aviv University, Israel; *B.R. Ilic*, National Institute of Standards and Technology

Micro- and nano-electromechanical systems (MEMS/NEMS) are among the most sensitive devices for detection of ultra-weak forces, masses, and

displacements. The small scale of these structures affords them very high frequencies (MHz to GHz), high quality factors, rich nonlinear phenomena, and many other beneficial traits that make them ideal as sensors and testbeds of fundamental physics. Fabry-Perot laser interferometry is a widespread and robust technique for probing MEMS/NEMS devices because it is non-invasive and provides exceptional motion sensitivity (≈ 1 pm/Hz^{1/2}) from DC to roughly 100 MHz. This technique utilizes the silicon substrate beneath the MEMS/NEMS device as a static reference mirror; doing so provides common-mode noise rejection in contrast to interferometers that use an external reference mirror. Furthermore, this technique is compatible with a wide range of MEMS/NEMS materials, from common insulators and conductors to graphene and other atomically-thin membranes.

Despite the many strengths of this experimental technique, it suffers from two main drawbacks. Firstly, the measured signal becomes highly nonlinear for device displacements larger than $\lambda/4$, where λ is the laser wavelength. Secondly, because the silicon backplane is immovable, there is no simple or established technique for calibrating device motion. As such, published results utilizing this setup typically report deflection in "arbitrary units." In this work, we focus on fully characterizing the nonlinear aspects of a MEMS/NEMS Fabry-Perot interferometer and developing a generalized approach to calibrate device motion based the wavelength of light. We will demonstrate how to quickly and accurately determine both static and dynamic MEMS/NEMS deflection by measuring reflected laser power in the time domain. We will further show how a single calibration (made in the large-amplitude regime) can be applied to subsequent measurements taken at lower amplitudes as well as to measurements taken in the frequency domain (e.g. by a lock-in amplifier). Lastly, we will demonstrate the capability of imaging the first three vibrational modes of a MEMS cantilever by using a scanning laser.

9:40am **NS+2D+AN+MN+MP+SE-WeM6 Silicon on Insulator Electrostatically Actuated Bistable Cantilevers for Resonant Displacement/Acceleration Sensing**, *O. HaLevy, E. Benjamin, N. Krakover, Y. Kessler, Slava Krylov*, Tel Aviv University, Israel

Resonant accelerometers incorporating vibrating beams demonstrate higher sensitivity and better robustness when compared to their statically operated counterparts. Electrostatic softening of the beams electrostatically coupled to the proof mass allows to enhance sensitivity of the resonant accelerometers. The displacement of the proof mass affects the gap between the mass and the beam and results in the beam's frequency change, which is maximal in the vicinity of the critical limit points of the voltage-deflection curve. The use of the snap-through buckling for this purpose is attractive since it is fully reversible and does not involve contact. While double-clamped curved bistable beams designed to demonstrate snap-through behavior can serve as resonant acceleration sensors [1], they suffer from high sensitivity to temperature and residual stress.

In this work we report on a design and fabrication of an electrostatically actuated bistable resonant cantilever [2], which demonstrates low sensitivity to the temperature and to the residual stress. The concept is based on the tailoring of the actuating force in such a way that the beam in its initial "as fabricated" configuration is positioned in the vicinity of the critical point. This is achieved by designing the actuating electrodes to be significantly thicker than the beam. Our reduced order (RO) Galerkin and coupled finite elements (FE) models results show that the frequency to deflection sensitivity of the $L = 150 \mu\text{m}$ long, $h = 16 \mu\text{m}$ wide and $d = 1 \mu\text{m}$ thick cantilever can reach 20 Hz/nm. This is equivalent to the frequency to acceleration sensitivity of 388 Hz/g, obtained for the case of a $4 \text{ mm} \times 4 \text{ mm} \times 20 \mu\text{m}$ proof mass.

While the model results are promising, fabrication of the device incorporating the beams and the electrodes of the different thicknesses is challenging. We demonstrate fabrication of the $50 \mu\text{m}$ thick electrodes and $\approx 6 \mu\text{m}$ thick cantilevers from the same device layer of a Silicon on Insulator (SOI) wafer. Two-stage deep reactive ion etching (DRIE) process was used for an initial patterning of the electrodes and of the cantilever and for the thinning of the beams. We discuss the details of the fabrication process and preliminary experimental results.

[1] N. Krakover, B. R. Ilic and S. Krylov, "Displacement Sensing Based on Resonant Frequency Monitoring of Electrostatically Actuated Curved Micro Beams," *J. Micromech. Microeng.*, **26**, pap. 115006, 2016.

[2] N. Krakover, S. Krylov, "Bistable Cantilevers Actuated by Fringing Electrostatic Fields," *ASME Journal of Vibration and Acoustics*, **139**(4), 040908-040908-10, 2017.

Wednesday Morning, October 24, 2018

11:00am **NS+2D+AN+MN+MP+SE-WeM10 Electron-Photon-Phonon Hybrid Systems Based on Compound Semiconductor Mechanical Resonators, Hiroshi Yamaguchi**, NTT Basic Research Laboratories, Nippon Telegraph and Telephone Corporation, Japan **INVITED**

The use of compound semiconductor heterostructures as the elastic materials in the fabrication of micro/nanomechanical resonators has advantages, such like the improvement of mechanical properties through strain engineering, optomechanical transduction through carrier-mediated coupling, and piezoelectrically controllable nonlinearity [1]. The hybrid properties play the essential role in the operation where the different excitations of phonons, photons, and electrons are mutually interacted. In this invited talk, I will review our recent activities studying the electronic [2], photonic [3], and phononic [4] functions in GaAs-based mechanical resonators.

[1] H. Yamaguchi, *Semicond. Sci. Technol.* 32, 103003 (2017).

[2] Y. Okazaki, I. Mahboob, K. Onomitsu, S. Sasaki, and H. Yamaguchi, *Nature Commun.* 7, 11132 (2016).

[3] H. Okamoto, T. Watanabe, R. Ohta, K. Onomitsu, H. Gotoh, T. Sogawa, and H. Yamaguchi, *Nature Commun.* 6, 8478 (2015).

[4] M. Kurosu, D. Hatanaka, K. Onomitsu, and H. Yamaguchi, *Nature Commun.* 9, 1331 (2018).

11:40am **NS+2D+AN+MN+MP+SE-WeM12 Size Dependent Mechanics of Elastomers, Le Li, N. Alsharif, K.A. Brown**, Boston University

Elastomers are fascinating materials owing to the fact that their mechanical properties are dictated by entropy. Due to their low modulus, chemical compatibility, and ease of processing, they are widely applied in fields from soft lithography to medical devices. While it is well accepted that they exhibit fascinating size-dependent mechanical properties when confined to thin films, the structure-property relationships that govern confined elastomers are difficult to unambiguously determine due to the mechanical influence of rigid support structures and unavoidable contributions from adhesion. As a result, a consensus regarding the moduli of elastomeric thin films has not emerged. Here, we present a combined computational and experimental approach to measure the true mechanical properties of thin elastomer films. First, we utilize extensive finite element simulations to determine a correction to the Hertzian contact model that depends upon a dimensionless film thickness and the polymer Poisson's ratio. In order to verify this correction, films composed of three different thermoplastics were studied using an atomic force microscopy (AFM) nanoindenting. Interestingly, all three were observed to soften when confined to films thinner than 100 nm, in agreement with literature reports of buckling experiments. To explore softer elastomeric materials that exhibit categorically different behavior, we extended this correction to the Johnson-Kendall-Roberts (JKR) model that considers adhesion in contact mechanics. Elastomer thin films with different crosslink densities were studied using AFM nanoindentation and finite element simulation to determine their moduli. We observed a drastic stiffening on all elastomeric films when they were confined to sub-micrometer thicknesses. More importantly, modulus of all sub-100 nm elastomer films converges to the same trend regardless of bulk crosslink density. We present a hypothesized molecular model explaining this behavior. These results shed new light on the nanomechanics of elastomers and provide a general process for exploring size-dependent mechanics in polymers.

Plasma Science and Technology Division

Room 104B - Session PS+AS+EL+EM+SE-WeM

Current and Future Stars of the AVS Symposium I

Moderator: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

8:20am **PS+AS+EL+EM+SE-WeM2 Invited Talk-Future Stars of AVS Session: Ellipsometry at THz Frequencies: New Approaches for Metrology and Metamaterial-based Sensing, Tino Hofmann¹**, University of North Carolina at Charlotte

Spectroscopic ellipsometry at terahertz frequencies has seen substantial advancements over the last several years. Now, instruments are available which allow precise measurements of the material's complex dielectric function including its anisotropy. This access to accurate electromagnetic material properties at THz frequencies is essential for the development of

increasingly advanced THz optical systems and a prerequisite for the design and manufacturing of optical elements for this spectral range.

In this talk I will give an overview of recent developments in the implementation of THz ellipsometry and focus on applications where THz ellipsometry contributed valuable material parameters. In combination with external magnetic fields generalized THz ellipsometry allows the accurate measurement of the optical Hall effect. The optical Hall effect enables the precise determination of the free charge carrier properties effective mass, mobility, and density in semiconductor heterostructures at THz frequencies without the need of electrical contacts and will be discussed in detail.

The exploration of novel physical phenomena observed in artificially structured metamaterials and the application thereof is of interest due to its relevance for the design and fabrication of novel THz optical elements and sensors. Metamaterials have attracted continued interest for almost two decades due to their unique electromagnetic properties, which can differ substantially from their constituents and often do not even exist in naturally occurring materials. We have demonstrated that although being orders of magnitude smaller than the probing wavelength, metamaterials composed of highly-ordered 3-dimensional metal nanostructures exhibit a strong anisotropic optical response at THz frequencies. I will discuss how these interesting optical properties may be used for novel THz sensor and device designs.

8:40am **PS+AS+EL+EM+SE-WeM3 Invited Talk-Future Stars of AVS Session: Remote Epitaxy – The Future for Stackable SiC Electronics, Rachael Myers-Ward²**, U.S. Naval Research Laboratory; *J. Kim*, Massachusetts Institute of Technology; *M.T. DeJarlid*, US Naval Research Laboratory; *K. Qiao*, *Y. Kim*, Massachusetts Institute of Technology; *S.P. Pavunny*, *D.K. Gaskill*, U.S. Naval Research Laboratory

Ideally, electronic heterostructures from dissimilar materials leads to enhanced functionality. Yet, experimentally forming these heterostructures is challenging due to lattice or thermal coefficient of expansion mismatch leading to defect formation or thermally driven atomic diffusion resulting in cross-doping and gradual junction transitions. These challenges may be overcome with the discovery of remote epitaxy and 2D layer transfer [1]. Here, SiC epitaxy is performed on epitaxial graphene as the electrostatic fields from the substrate penetrate the graphene and guide adatom registry. The film is easily peeled away since the graphene is not bonded to either the substrate or epilayer; the epilayer is then van der Waals bonded to a different material enabling new functionality. We will present experimental results on the remote epitaxy of SiC, illustrating potential quantum science applications.

There are three necessary steps to create remote epitaxy. The first is to grow epitaxial graphene on SiC, followed by transferring the graphene to a desired substrate (if different from SiC), and finally the growth of the remote epitaxial layer. If the remote epitaxy is to be SiC, which is the focus of this paper, the second step is not needed. Epitaxial graphene (EG) was first synthesized on 4H- and 6H-SiC in a horizontal hot-wall CVD reactor between 1540 and 1580 °C in 10 slm of Ar and 100 mbar [2]. The growth temperature was dependent upon the offset of the substrate, where substrates with higher offsets require a lower growth temperature to ensure 1 ML of EG, which is desired to assist in SiC adatom registry during growth. SiC remote epitaxy was then performed on the EG using silane (2% in H₂) and propane precursors, where the SiC polytype replicated the underlying substrate. In an effort to transfer the remote SiC epi/EG to another substrate such as SiO₂/Si, a metallization step was performed. Thin Ti and/or Ni layers were initially deposited followed by a thicker high stress metal to create strain and aid in removing the remote SiC epi/EG from the SiC substrate [1]. Once transferred, the metal was removed via a metal etch.

In this work, we will discuss the important parameters needed for successful remote SiC epitaxy, such as metallization, graphene thickness and remote epitaxy growth temperature. The epitaxial morphology characterized by SEM and Nomarski microscopy and graphene coverage and transfer evaluated by Raman spectroscopy will be presented.

[1] Kim, *et al.*, *Nature* 544, 340 (2017).

[2] L.O. Nyakiti, *et al.*, *MRS Bulletin* 37, 1150 (2017).

¹ Future Stars of the AVS

Wednesday Morning, October 24, 2018

² Future Stars of the AVS

Wednesday Morning, October 24, 2018

9:00am **PS+AS+EL+EM+SE-WeM4 Invited Talk-Future Stars of AVS Session: Low-Temperature Growth for 3D Integration of van der Waals Materials, Christopher L. Hinkle¹**, University of Texas at Dallas

The integration of novel logic and memory devices, fabricated from van der Waals materials, into CMOS process flows with a goal of improving system-level Energy-Delay-Product (EDP) for data abundant applications will be discussed. Focusing on materials growth and integration techniques that utilize non-equilibrium, kinetically restricted strategies, coupled with in-situ characterization, enables the realization of atomic configurations and materials that are challenging to make but once attained, display enhanced and unique properties. These strategies become necessary for most future technologies where thermal budgets are constrained and conformal growth over selective areas and 3-dimensional structures are required.

In this work, we demonstrate the high-quality MBE heterostructure growth of various layered materials by van der Waals epitaxy (VDWE). The coupling of different types of van der Waals materials including transition metal dichalcogenide thin films (e.g., WSe₂, WTe₂, HfSe₂), helical Te thin films, and topological insulators (e.g., Bi₂Se₃) allows for the fabrication of novel electronic devices that take advantage of unique quantum confinement and spin-based characteristics. We demonstrate how the van der Waals interactions allow for heteroepitaxy of significantly lattice-mismatched materials without strain or misfit dislocations. We will discuss TMDs, Te, and TIs grown on atomic layer deposited (ALD) high-k oxides on a Si platform as well as flexible substrates and demonstrate field-effect transistors with back-end-of-line (<450 °C) and even flexible plastics (<200 °C) compatible fabrication temperatures. High performance transistors with field-effect mobilities as high as 700 cm²/V-s are demonstrated. The achievement of high-mobility transistor channels at low processing temperatures shows the potential for integrating van der Waals materials into new technologies.

This work was supported in part by the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA. This work is also supported in part by NEWLIMITS, a center in nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041.

9:20am **PS+AS+EL+EM+SE-WeM5 Invited Talk-Future Stars of AVS Session: Engineering the Properties at Heusler Interfaces, Jason Kawasaki²**, University of Wisconsin - Madison

The Heusler compounds are a ripe platform for engineering and discovering emergent electronic, magnetic, topological, and ferroic properties at crystalline interfaces, either with other functional Heuslers or with compound semiconductor or oxide substrates. In these applications, the ability to control interfaces with near atomic level control is of tantamount importance; however, challenges such as interdiffusion have hampered their development. Here, I will discuss our efforts to control the properties of Heusler interfaces using precision growth by molecular beam epitaxy (MBE). Results will be presented in three areas: (1) the use of epitaxial strain to stabilize the hexagonal phase of several polar metal candidates, (2) the use of monolayer graphene diffusion barriers to enable high temperature growth and performance of spintronic devices, and (3) the phase segregation of ferromagnetic FeV nanostructures from a semiconducting FeVsb matrix with coherent epitaxial interfaces. Together, these examples illustrate the power of epitaxy and interfaces in controlling the properties of Heuslers and other intermetallic compounds, and integrating them onto commonly used semiconductor substrate platforms.

9:40am **PS+AS+EL+EM+SE-WeM6 Invited Talk-Future Star of AVS Session: Atom Probe Tomography for 3D Semiconductor Devices Applications, Ajay Kumar Kambham³**, GLOBALFOUNDRIES U.S. Inc.

Device structures are rapidly scaling down to the nanometer regime with the ongoing development in semiconductor device technology. Along with this, it is ever critical need to engineer dopant profiles and to define the formation of junctions in Metal-oxide field effect transistors (MOSFETs). This is increasingly challenging considering the severity of short channel effects (SCEs). Indeed, one type of SCE in MOSFET devices known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity, fully depleted silicon-on-

insulator (FDSOI) structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the role of APT and how elemental distributions vary depending on process conditions along with the challenges involved in sample preparation.

11:00am **PS+AS+EL+EM+SE-WeM10 Invited Talk-Future Stars of AVS Session: Three-Dimensional Imaging of Complex Oxide Interfaces, Divine P. Kumah⁴**, North Carolina State University

Complex oxide materials have a wide range of exciting tunable electronic and magnetic phases including ferroelectricity and superconductivity. The ability to fabricate atomic layers of complex oxides has led to the formation of novel interfaces and heterostructures of scientific and technological interest. The functional properties are usually correlated to sub-Angstrom structural perturbations at these interfaces. In this talk, a non-destructive synchrotron X-ray three-dimensional imaging technique will be applied to understand thickness-dependent electronic and magnetic transitions which occur in rare-earth manganite films with thicknesses on the order of an atomic layer. We show that structural distortions arising due to the electrostatic interfacial boundary conditions of the thin films are related to their thickness-dependent phase transitions. Based on these results, we show that heterostructures can be designed by molecular beam epitaxy to tune the atomic-scale structure of the manganite films to achieve robust ferromagnetism in atomically-thin layers. These results have important implications for the design of oxide-based spintronic devices and provide an important pathway for the realization of novel functional materials.

11:20am **PS+AS+EL+EM+SE-WeM11 Invited Talk-Future Stars of AVS Session: Illuminating Physics of Magnetron Sputtering Discharges, Matjaz Panjan⁵**, Jozef Stefan Institute, Slovenia

Magnetron sputtering is an established plasma technology for the deposition of thin films. In general, the technique is classified by the voltage supplied to the cathode; this can be continuous (DCMS), pulsed (HiPIMS) or oscillatory (RFMS). The distinction is also made with respect to the geometry of the magnetron source (e.g., circular, linear, cylindrical) and the magnetic field configuration (balanced or unbalanced). Despite the differences in the cathode operation, geometry and, magnetic field configuration, the underlying principle that forms dense magnetron plasma is the same. The central feature of magnetron sources is a crossed magnetic and electric field arrangement, which captures electrons close to the cathode. In such configuration, electrons gyrate around the magnetic field lines, bounce from the electric field of the sheath and drift in the azimuthal direction. The entrapment of electrons increases the plasma density close to the cathode (e.g., forming a ring-shaped plasma above the circular magnetron) and enhances the sputtering rate. Experiments using high-speed imaging and other techniques revealed that magnetron plasma is not azimuthally homogenous instead, it forms dense plasma structures called spokes. These structures have been extensively studied over the past few years and have changed our understanding of several physical processes in the magnetron discharges.

Spokes are observed for a wide range of discharge conditions, magnetron geometries and are an essential feature of all operational regimes [1-3]. They commonly form periodic patterns, have an arrowhead-like shape with an arrow pointing in the $\mathbf{E} \times \mathbf{B}$ direction, and travel with azimuthal velocities of several km/s. In the talk, I will present efforts to understand the physics of spokes and magnetron discharges in general. In particular, I will discuss spatial distribution of the plasma potential [4] and the influence it has on the transport of charged particles [5], sputtering process and overall sustainability of the discharge. I will demonstrate that electric fields associated with spokes cause localized re-energization of electrons and thus help to sustain magnetron discharge. Spokes also influence energy and spatial distribution of ions and therefore indirectly affect the thin film growth.

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¹ Future Stars of the AVS

² Future Stars of the AVS

³ Future Stars of the AVS

⁴ Future Stars of the AVS

⁵ Future Stars of the AVS

11:40am PS+AS+EL+EM+SE-WeM12 Peter Mark Memorial Award: Plasma-bio Interactions: Investigating Mechanisms to Enable New Applications, Peter Bruggeman¹, University of Minnesota **INVITED**

Cold non-equilibrium atmospheric pressure plasmas (CAPs) have received a lot of attention in the last decades due to their huge potential for biomedical applications including wound healing, cancer treatment, dental treatments and disinfection and decontamination of heat sensitive materials [1]. These applications are due to the near ambient gas temperature at which CAPs can be produced and their high reactivity, involving the production of numerous reactive oxygen and nitrogen species [2]. Many applications require controlled interactions of plasma with bacteria, virus and mammalian cells or tissue that enable selectivity between healthy and cancer cells or in the treatment of bacteria on healthy tissue or food samples for which off target effects needs to be minimized. A controlled selectivity might be the greatest challenge for these applications and requires a detailed understanding of the underlying plasma-bio-interaction mechanisms. In this framework, my group in collaboration with microbiologists has performed detailed studies of the interactions of CAP with virus, bacteria and mammalian cells. Our research shows that controlling the gas phase plasma chemistry can lead to significant different biological responses of the living organisms [3-6]. The outcomes of these studies allow unraveling chemical pathways responsible for plasma-bio interactions and linking plasma kinetics to plasma-bio interactions. These insights are of invaluable importance for the development of applications in the field of plasma medicine.

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Acknowledgements

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Applied Surface Science Division Room 204 - Session AS+SE-WeA

Industrial and Practical Applications of Surface Analysis

Moderators: Jeffrey Fenton, Medtronic, Svitlana Pylypenko, Colorado School of Mines

2:20pm **AS+SE-WeA1 Identification of Unknown Contaminants in Industrial Applications Using MS/MS in Combination with High Resolution Mass Spectrometry**, A. Pirkl, Julia Zakel, D. Rading, IONTOF GmbH, Germany; N.J. Havercraft, IONTOF USA; S. Kayser, H. Arlinghaus, R. Moellers, E. Niehuis, IONTOF GmbH, Germany

The fast and reliable characterisation of unknown contaminants in quality control procedures is crucial in many industrial areas to understand manufacturing errors and avoid production downtime. TOF-SIMS nowadays plays an important role in this area especially due to its fast imaging capabilities that enable the acquisition of chemical surface images with a lateral resolution in the 100 nm range.

However, molecular identification of unknown substances can be hampered by constraints in mass resolution and mass accuracy of a standard TOF analyser. To overcome this problem, we have developed a new Hybrid SIMS instrument, which uniquely combines all advantages of a state-of-the-art TOF-SIMS with the mass spectrometry performance of an Orbitrap mass analyzer (Q Exactive™ HF) [1]. The Q Exactive mass spectrometer provides a mass resolution of more than 240,000 @ $m/z = 200$, sub ppm mass accuracy, and fully integrated MS/MS capabilities that allow low energy collision induced fragmentation for structural analysis of complex molecules. All in all this dramatically increases the level of confidence for the SIMS analysis.

Different applications ranging from polymers to metals will be presented with a focus on the identification of unknown substances by MS/MS in combination with high resolution mass spectrometry. Furthermore dedicated measurement modes and strategies that can be applied to different forms of contaminants will be presented. The use of databases will be showcased which further assists and confirms the results of a manual data evaluation.

[1] The 3D OrbiSIMS – Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolving Power, Passarelli et al., Nature Methods, 2017, 14(12):1175-1183, DOI 10.1038/nmeth.4504.

2:40pm **AS+SE-WeA2 ToF-SIMS Analysis of Glass and Glass Coatings**, **Christine Mahoney**, Corning Inc.

Many think of glass as being an inert material. However, glass contains many reactive alkalis and other elements that can interact and diffuse into solutions or into coatings. These alkalis tend to decrease the chemical durability of the glass itself, and can play a key role in accelerating corrosion and delamination mechanisms involving the glass. How we manufacture and process the glass plays a significant role in its chemical durability and reactivity. The reactivity of a glass surface can be particularly problematic for pharmaceutical applications, where glass delamination in vials and/or drug interactions with glass constituents can potentially occur. Here we present an overview of ToF-SIMS research at Corning involving the analysis of glass surfaces and their associated coatings. Both organic and inorganic applications will be discussed, using a wide range of tools for analysis.

3:00pm **AS+SE-WeA3 Problem Solving with Valence Band Spectroscopy and SIMS MS/MS**, **Steven Pachuta**, D.M. Poirier, 3M Company **INVITED**

Surface chemistry is often key to the performance of materials like films, coatings, and adhesives. Controlling and understanding surface chemistry is therefore critical to manufacturers. X-ray photoelectron spectroscopy (XPS) is the workhorse in industrial surface characterization laboratories, followed closely by time-of-flight secondary ion mass spectrometry (ToF-SIMS). XPS survey spectra provide quantitative elemental information on surfaces, and XPS high energy-resolution spectra can give information on chemical states. ToF-SIMS, in general, gives even more specific surface chemical information, such as the identities of polymer additives and surface contaminants.

This presentation will describe efforts to increase the chemical specificity of both XPS and ToF-SIMS for organic species, especially polymers. The XPS valence band region contains a complex fingerprint which is highly dependent on molecular structure. By using databases in combination with multivariate methods such as principal component analysis (PCA) and

partial least squares (PLS), a surprising degree of information can be extracted from valence band spectra of unknown materials.

The fact that many real-world surfaces comprise a mixture of components is a recurrent frustration in industrial surface characterization. ToF-SIMS analysts have long envied their GC/MS and LC/MS counterparts, who have the luxury of separating mixtures before doing mass spectrometry. The recent commercial availability of tandem mass spectrometry (MS/MS) on ToF-SIMS instruments has gone some way towards addressing the mixture problem and has increased the ability of ToF-SIMS to identify unknown materials. Examples will be presented.

4:20pm **AS+SE-WeA7 Surface and In-depth XPS Characterization of Liquid and Cured Control Release Additives (CRAs) Used in Silicone-Based Release Coatings**, **Brian Strohmeier**, K. Rhodes, R. Muniget, J. Orłowski, Avery Dennison Corporation

Silicone-based release coatings are used in a wide variety of commercial applications including: release liners for removable pressure sensitive adhesive laminates and tapes, release papers and polymer films, non-stick packaging, and other products where a specific force of peel separation is required between two different film materials during processing or storage. Typical industrial silicone-based release coatings consist of UV or heat cured mixtures of silicone compounds and controlled release additives (CRAs). CRAs commonly contain proprietary mixtures of functionalized silanes, siloxanes, and silica, plus a variety of other organic components. The release properties of silicone-based release coatings depend highly on the distinct types and relative amounts of the silicone compounds and CRAs used in the cured mixture. Therefore, it is of great interest to quantitatively characterize the silicone and CRA components on the surface of silicone release coatings for improved product and process development as well as problem-solving related to release issues. In this study, a variety of commercial CRA products were characterized by gel permeation chromatography (GPC) for bulk molecular weight distribution information and by X-ray photoelectron spectroscopy (XPS) for surface composition and chemistry. The CRA materials studied had vapor pressures that allowed successful XPS characterization in the liquid state. Surprisingly, the CRA liquids could even be sputtered and/or depth profiled using argon cluster ions, whereas sputtering with monatomic argon ions resulted in XPS chemical state changes caused by ion beam induced sample damage. The CRA materials were characterized by XPS and argon cluster ion sputtering/depth profiling in the pure liquid state and in solid heat cured release coating mixtures with polydimethyl siloxane (PDMS). The high resolution Si 2p XPS spectra obtained for cured silicone release coatings of known composition could be peak-fitted into separate CRA and PDMS components to produce a quantitative calibration curve for evaluating release coatings with unknown CRA/silicone compositions.

4:40pm **AS+SE-WeA8 Differentiating Silicones Using SIMS**, **Paul Vlasak**, M.L. Pacholski, The Dow Chemical Company

The unique properties of poly(dimethylsiloxane), also known as PDMS or silicone, have allowed PDMS-based materials to proliferate in modern industry. A huge variety of applications using PDMS have been developed including structural adhesives, release agents, optical components, lubricants, anti-foam agents, and potting agents to name a few. Considering the omnipresence of PDMS in industrial settings along with its low surface energy and tendency to migrate, it comes as no surprise that PDMS is frequently encountered in industrial surface analysis laboratories. Because PDMS is readily detected and easily recognized by its characteristic fragmentation pattern, SIMS is well suited to identifying the presence of silicones on a wide range of materials.

In some instances, the analyst expects to find PDMS on a sample surface. For example, the PDMS transferred from a silicone release liner onto an adhesive may be of interest. In other instances, PDMS can be encountered as an unexpected contaminant, perhaps interfering with adhesion or causing defects in a coating or painting operation. In either case, besides its mere presence, the structural details of the PDMS may be important to understanding the behavior of the adhesive/release system or discovering the actual source of a contaminant amongst multiple possibilities.

From a pragmatic standpoint, the current work explores how molecular weight, endgroup type, and other structural factors influence PDMS fragmentation patterns through the use of well-characterized reference materials. The effects of instrument-related parameters as well as film thickness and substrate type will also be considered to the extent these factors influence the spectra obtained.

Wednesday Afternoon, October 24, 2018

5:00pm **AS+SE-WeA9 Uranium Particles Analysis and Imaging Using ToF-SIMS for Source Identification**, *Juan Yao, E. Krogstad, S. Shen, Z.H. Zhu, X-Y. Yu*, Pacific Northwest National Laboratory

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a highly surface sensitive analytical tool. It offers excellent limits of detection (LODs) of part per million with sub-micron spatial resolution. Besides determining isotopic ratios of radioactive materials, ToF-SIMS has the advantage of providing full mass spectra with m/z up to 2000 Da, allowing the detection of chemical signatures in a material. This latter feature is very attractive to identify the source of uranium and other radioactive materials in single particles. We analyzed three different NIST standard reference materials with varied concentrations of uranium in this study. Samples are in the form of glass wafers and particles deposited on a substrate. By applying spectral principal component analysis (PCA), the SIMS mass spectra obtained from the same type of NIST sample show consistent features; regardless of the sample form. Furthermore, a blind test was conducted using a mixture consisting of particles from all three NIST materials. Our spectral PCA results illustrate that ToF-SIMS can be a useful tool to differentiate particles of different origins and potentially applicable for signature identification in single particles. In addition, scanning electron microscopy (SEM) was applied to complement the SIMS imaging for correlative analysis [1]. It is beneficial to use SEM to obtain particle morphological information. However, SEM lacks the sensitivity in single particle elemental analysis compared to ToF-SIMS. Our work demonstrates that ToF-SIMS is a powerful tool for analysis of individual radioactive particles to fulfill nuclear safeguards and forensic missions.

5:40pm **AS+SE-WeA11 Application of X-ray Photoelectron Spectroscopy to Degradation Studies of Electrodes in Fuel Cells and Electrolyzers**, *Kateryna Artyushkova*, University of New Mexico; *N. Danilovic*, Lawrence Berkeley Lab, University of California, Berkeley; *C. Capuano*, Proton on site; *A. Serov*, Pajarito Powder LLC; *P. Atanassov*, University of New Mexico

The stability of materials used in anodes and cathodes in fuel cells and electrolyzers is a critical factor for practical industrial applications. To improve the longevity, it is important to link the chemical structure to degradation mechanisms and changes in the surface composition of the catalyst on the electrodes. Application of x-ray photoelectron spectroscopy (XPS) to probe structure of catalytic materials and their degradation is becoming an important analytical approach due to its accessibility and quantitative chemical information provided. This talk will present several examples of application of high-resolution XPS for analysis of the chemistry of electrodes and changes that are occurring during operation in several technological platforms, such as proton-exchange membrane fuel cells (PEMFCs), alkaline membrane fuel cells (AEMFC), direct methanol fuel cells (DMFC), direct hydrazine fuel cells (DHFC) and water electrolyzers (WE).

Applied Surface Science Division Room 204 - Session AS+SE-ThM

Applied Surface Analysis of Novel, Complex or Challenging Materials

Moderators: Michael Brumbach, Sandia National Laboratories, Thomas Grehl, IONTOF GmbH, Germany

8:00am **AS+SE-ThM1 Understanding the Surface of Complex Oxides used in High Temperature Electrochemical Devices**, *John Kilner*, Imperial College London, UK; *J.W. Druce*, International Institute for Carbon Neutral Energy Research (I2CNER), Japan; *H. Tellez*, *A. Staykov*, International Institute for Carbon Neutral Energy Research (I2CNER)

INVITED

High temperature electrochemical devices, such as solid oxide fuel cells and electrolyzers, have been under development for application in clean energy systems for many years. Although acceptable performance can be achieved, the requirements of low cost and high durability have been a major hurdle to commercialization. This has necessitated a lowering of the operating temperature from circa 800-900°C, to temperatures in the region of 500-600°C, with a consequent loss of electrochemical activity of the electrodes, particularly the air electrode. Key to optimizing performance is gaining an understanding of the gas/solid interface between the Mixed Ionic Electronic Conducting (MIEC) electrodes and the oxygen-rich ambient, and how the structure, composition and activity evolves with time. We have used a multifaceted approach to probe the surfaces of ceramic mixed conductors, after treatment in typical SOFC cathode operating conditions. This has involved ion beam based techniques such as Low Energy Ion Scattering (LEIS) to sample the composition of the outermost atomic layers of ceramic materials, Secondary Ion Mass Spectrometry (SIMS) to measure oxygen exchange activity, complemented by Density Functional Theory (DFT) to clarify possible mechanisms.

The surface termination of substituted (AA')(BB')O₃ perovskite-based MIEC materials, such as La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF), has been studied using LEIS [1] and shown to be dominated by A cations and oxygen, and in particular by segregation of the Sr substituent. For selected (AA')(BB')O₃ compositions, we have investigated the rate of oxygen exchange and shown changes in surface activity that are related to changes in surface chemistry. We have used the knowledge gained from experiment to guide theoretical investigations, to aid in the optimization of candidate air electrode materials. This theoretical study was performed using DFT to simulate the interaction of an oxygen molecule with representative AO and A'O segregated surfaces [2,3].

This combination of theoretical studies guided by advanced surface analysis techniques (i.e. LEIS and SIMS) is enhancing our understanding of processes which determine the performance of these important clean energy devices.

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8:40am **AS+SE-ThM3 Vectorial Method used to Monitor a XPS Evolving System: Titanium Oxide Thin Films under UV Illumination**, *S. Bechu*, Institut Photovoltaïque d'Ile-de-France; *N. Fairley*, Casa Software Ltd, UK; *L. Brohan*, Institut des matériaux Jean Rouxel, France; *Vincent Fernandez*, Université de Nantes, Institut des matériaux Jean Rouxel, France; *M. Richard-Plouet*, Institut des matériaux Jean Rouxel, France

1. Introduction

Third generation solar cells aims at increasing efficiency to overtake the 31% theoretical efficiency of simple junction photovoltaic cells established by Shockley and Queisser. According to Marti and Luque [1], intermediate band cell concept could increase the photocurrent via the absorption of sub-bandgap photons without degrading the voltage. In this perspective, we developed hybrid photosensitive sols-gels based on titanium complexes with specific optical and electronic properties [2]. Once illuminated under UV light, an intermediate band (IB) appears in the band structure so the absorption spreads over visible to near infrared due to reduction of Ti(IV) in Ti(III) [3] and leads to several important changes in the titanium oxide

based nanomaterial chemistry. Thanks to this absorption range increase, these gels could be used as active layers in solar cells.

2. Analysis applied to characterize chemical modifications

In order to get insight in the chemical modifications induced by the creation of the IB, XPS experiments were conducted on thin films while UV illumination was performed *in situ*. We present here a new mathematical method which can be applied to XPS measurements when an evolving set of data is recorded: the vectorial method [4,5]. In this case this method is applied simultaneously to Ti 2p and O 1s XPS peaks [6]. From the data set analysis, we established that each of the two Ti(IV) and Ti(III) signals can be split into two components: one Ti(IV) at 458.4 eV is associated to one Ti(III) at 457.1 eV whereas, under UV illumination, a second Ti(IV) peak appears and evolves similarly than a second Ti(III) peak, at 458.1 and 456.7 eV respectively. Those features were obtained from the vectorial method. It was successfully applied to *in situ* UV illumination allowing to get the percentage of thin films photoreduction, the chemical state appearing upon illumination and evolution.

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9:00am **AS+SE-ThM4 XPS Characterization of Copper and Silver Nanostructures**, *Tatyana Bendikova*, *M.D. Susman*, *F. Muench*, *A. Vaskevich*, *I. Rubinstein*, Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials in terms of elemental composition, chemical and electronic states of the elements and thin layer thicknesses. Here we present examples where XPS analysis provides critical information for understanding the growth and oxidation mechanisms of metal nanostructures.

Studies of solid-state oxidation of copper nanoparticles (NP) by in-situ plasmon spectroscopy complemented by electron microscopies showed formation of oxide/(metal+void) core-shell structure.¹ XPS analysis allows us to unambiguously identify the presence of both CuO and Cu₂O phases in the oxide shell, and to calculate the relative thicknesses of each layer. These data, in combination with electrochemistry, provide proof for a quantitative model of Cu NPs oxidation.

In a recent study, we investigated the mechanism of the electroless formation of nanostructured silver nanoplatelet (NPL) films in the presence of a Fe(III)-tartrate complex.² Electron microscopy and XRD showed that NPLs are formed by secondary nucleation on the edges, while nucleation on the flat (111)-oriented faces is suppressed. XPS analysis of NPLs confirmed strong Fe(III)-tartrate adsorption to the Ag NPS surface. XPS studies of the Fe chemical environment reveal the possible formation of polymeric complexes in the adsorbed layer, which may explain the almost complete inhibition of secondary nucleation on the flat (111) surfaces of Ag NPLs.

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- *Prof. Israel Rubinstein deceased on October 21, 2017.

9:20am **AS+SE-ThM5 Quantification of Hydroxyl, Major Element and Trace Element Concentrations in Oxide Glasses by Quadrupole SIMS.**, *Albert Fahey*, *A.R. Sarafian*, *T. Dimond*, Corning Inc.

Major and trace element calibrations have been established for positive and negative secondary ions measured by Quadrupole SIMS. A Cs⁺ primary ion beam is used exclusively and element secondary ions are measured directly, not by the MCs⁺ method. This affords greater sensitivity and is

Thursday Morning, October 25, 2018

better matched to the operating characteristics of a quadrupole mass spectrometer than by using MCs+ for positive ion species only. Both natural well-studied geologic glasses and Corning research glasses that have been thoroughly characterized have been used to establish the calibrations.

The CAMECA 4550 Quadrupole SIMS is well-suited to measurement of oxide glasses. Charge-compensation is easily achieved for a Cs+ primary beam on uncoated samples of almost any size. This allows the measurement of concentration of species in the surface of glass (from a few nanometers to several micrometers) that can have a significant impact on the physical and chemical durability of the glass. Because oxide glasses contain oxygen as their major element both positive and negative ions can be generated by sputtering with Cs. Although the use of a Cs primary ion beam is generally associated with measurement of negative secondary ions or the use of MCs+ secondary ions, the presence of oxygen in the glass allows production of a significant quantity of positive ions yielding linear calibrations for species that typically would produce positive secondary ions with an oxygen primary beam. Of course, secondary negative ions are produced as well and for the appropriate elements and small molecular ions yield linear calibrations as well.

Detection limits and details of the calibrations will be shown and discussed and examples-measurements of near surface composition changes in various oxide glasses will be shown. Connections of surface chemistry to other glass-properties will be made and explained.

9:40am AS+SE-ThM6 Modification of Sputtered Carbon Surfaces in Biosensor Arrays, Varun Jain, M.R. Linford, Brigham Young University

We describe the chemical modification of carbon surfaces with an eye towards employing them in biosensor (DNA) arrays. Carbon was deposited in thin film form by DC and HIPIMS magnetron sputtering. These depositions were confirmed by atomic force microscopy step height measurements. As indicated by X-ray photoelectron spectroscopy (XPS), the resulting material contained some oxidized carbon at its surface, including -COOH type moieties. These groups could be directly activated for amine attachment using a combination of a carbodiimide (EDC) and sulfo -N-hydroxysuccinimide. Direct attachment of a variety of amines was then possible on this surface, where this process could be followed through the N 1s XPS signal. The surfaces were also activated by direct chlorination using PCl₅, where this process could again be followed by XPS - XPS revealed the introduction and disappearance of chlorine. That is, the chlorine on the resulting carbon surfaces could be nucleophilically replaced with a variety of amines. The DC and HIPIMS sputtered carbon films showed different numbers of reactive functional groups, and the HIPIMS carbon shows unusually smoothness and density by scanning electron microscopy.

11:00am AS+SE-ThM10 The Role of Surface Analysis in Characterization of Synthetic Opioids: TOF-SIMS imaging of Fentanyl and Fentanyl Analogs for Forensics and First Responder Safety, Greg Gillen, S. Muramoto, J. Verkouteren, E. Sisco, National Institute of Standards and Technology (NIST)

The misuse and addiction to opioids including heroin and synthetic opioids such as fentanyl and its various analogs has become a national crisis. Drug overdoses have become the leading cause of death for Americans under the age of 50 with 64,000 overdose related deaths in 2016. The extreme potency of fentanyl and its analogs (100-10,000 times more potent than morphine) may result in even very small doses causing life threatening overdoses. The potency is also a safety concern due to the potential for accidental exposure of law enforcement, first responders, forensic lab personnel and health care providers. To address this concern, several trace chemical analysis techniques are being evaluated as presumptive methods for identification of a suspected opioid while minimizing exposure to end users (1). In addition, since the bulk of illicitly manufactured fentanyl enters the US via overseas mail, there is interest in application of the same chemical screening techniques for detection of fentanyl residues on packages to support interdiction. To facilitate the continued development, evaluation and optimization of the aforementioned screening tools, TOF-SIMS imaging and mass spectral analysis is being used to characterize the particle size and chemical composition of fentanyl and related compounds produced by solution casting of pure materials onto metal substrates or as particles collected on conductive adhesive tapes after sampling the outsides of packages containing suspected opioids. TOF-SIMS was able to image and provide unique mass spectral signatures from individual particles of heroin, fentanyl and several analogs. In order to increase the sensitivity of TOF-SIMS for particle identification, we have evaluated the use of acidic polymer substrates (Nafion) as proton donating particle collection substrates. Preliminary results suggest orders of magnitude

improvements in protonated secondary ion signals for fentanyl. Finally, the screening technologies being developed were not designed with consideration of the significant toxicity of fentanyl and fentanyl analogs in the form of respirable aerosols. In a typical screening analysis, thermal desorption from a collection swipe can lead to the formation of aerosols in micrometer size range posing a possible risk of toxic exposure to the analyst. TOF-SIMS was also used to characterize the size distribution of thermally desorbed aerosols emitted by these techniques.

- (1). Edward Sisco, Jennifer Verkouteren, Jessica Staymates and Jeffrey Lawrence, *Forensic Chemistry*, (4), 108-115 (2017).

11:20am AS+SE-ThM11 3D TOF SIMS, Parallel Imaging MS/MS, and XPS Analysis of Glitterwing (*Chalcopteryx rutilans*) Damselfly Wings, Ashley Ellsworth, D.M. Carr, G.L. Fisher, B.W. Schmidt, Physical Electronics; W.W. Valeriano, W.N. Rodrigues, UFMG, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) damselfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for damselflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C₆₀⁺ and large cluster Ar_n⁺. With the recent addition of MS/MS capabilities, a conventional TOF-SIMS (MS1) precursor ion analysis and tandem MS (MS2) product ion analysis of targeted precursor ions may be acquired simultaneously and in parallel. The parallel imaging MS/MS is a powerful tool allowing for unambiguous peak identification and provides the maximum information from a given analytical volume.

Here, we explore the use of MS/MS to characterize the chemical composition of the waxy cuticle present on the outer surface of the damselfly wing. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals. [2] Further, we will compare and contrast XPS large cluster Ar_n⁺ depth profiling results to reveal the complementary nature of the two techniques.

- [1] W.W.Valeriano, Masters dissertation, UFMG, 2016. Retrieved from http://www.fisica.ufmg.br/posgrad/Dissertacoes_Mestrado/decada2010/wesley-valeriano/WesleyWalisonValeriano-diss.pdf.

- [2] D. M. Carr, A. A. Ellsworth, G. L. Fisher, et al., Characterization of natural photonic crystals in iridescent wings of damselfly *Chalcopteryx rutilans* by FIB/STEM, TEM, and TOF-SIMS, *Biointerphases* 13 (2018), 03B406.

11:40am AS+SE-ThM12 Characterization of Aniline Dyes in the Modern Colored Papers and the Prints of José Posada, J.K. Hedlund, L.D. Gelb, Amy Walker, University of Texas at Dallas

José Posada was a Mexican artist active during the turn of the 20th century, and is often called the father of modern Mexican printmaking. Many of his prints ("broadsides") have vivid colors but are in urgent need of repair. The dyes that give these broadsides their colors are aniline dyes which are soluble in many solvents. Solvents are often used in paper conservation for the removal of pressure-sensitive tapes, and so treatment protocols that preserve these colors are needed. To develop these methods the aniline dyes need to be identified and characterized.

Dye identification requires either non-destructive *in situ* techniques, such as Raman spectroscopy, or *ex situ* techniques with very high sensitivity; only extremely small samples can be taken in order to preserve the integrity and appearance of the broadsides. Although Raman spectroscopy has been employed to analyze Posada prints it has only limited success especially in the analysis of blue and yellow dyestuffs.

We present a new strategy for analyzing dyed paper samples using secondary ion mass spectrometry (SIMS) and analysis of the resulting data using maximum *a posteriori* (MAP) reconstruction. To test our protocol, we first characterized modern cotton paper colored with a range of aniline

Thursday Morning, October 25, 2018

dyes. Subsequently we analyzed fiber samples taken from Posada prints. Using SIMS, we are able to identify the dyes used in Posada prints, including hitherto unidentified blue and yellow dyes. Furthermore, MAP analysis provides not only unambiguous identification of the dye adsorbed in the paper by comparison with pure-dye reference samples, but also the characteristic mass spectrum of the paper itself.

12:00pm **AS+SE-ThM13 GaAs and Si Surface Energies derived from Three Liquid Contact Angle Analysis (3LCAA), as a Function of Oxygen Coverage for Heterogeneous Nano-Bonding™**, *Sukesh Ram*, Arizona State University; *K.L. Kavanagh*, Simon Fraser University, Canada; *F.J. Ark, C.E. Cornejo, T.C. Diaz, M.E. Bertram, S.R. Narayan, J.M. Day, M. Mangus, R.J. Culbertson, N. Herbots*, Arizona State University; *R. Islam*, Cactus Materials, Inc.

Native oxides used as surface passivation during semiconductor processing hinder the formation of high quality epitaxial layers. In this research, the surface energies and oxygen content of native oxides of Si(100) and GaAs(100) are measured before and after surface processing prior to a wafer bonding process at $T < 220^\circ\text{C}$, "NanoBonding™" [1,2]. Based on Van Oss's theory, Three Liquid Contact Angle Analysis (3LCAA) yields the total surface energy, γ^T , of semiconductors and insulators. Van Oss models γ^T as combining of molecular interactions or "Lifshitz-Van der Waals" energy γ^{LW} with the energy of interaction with electron donors, γ^+ , and acceptors, γ^- . A new automated image analysis algorithm, "Drop and Reflection Operative Program" (DROP), enables fast, accurate and reproducible extraction of contact angles without subjectivity, reducing to $< 1^\circ$ the typical $\sim 5^\circ$ error between contact angles measurements due to manual extraction. Using for each wafer, a minimum of 12 to 30 drops yields 48 to 120 contact angles, yielding γ^T , γ^{LW} , γ^+ and γ^- with accuracies better than 3%. By using Ion Beam Analysis (IBA) combining $< 111 >$ channeling in (100) crystals with the 3.039 ± 0.01 MeV (^{16}O , ^{18}O) nuclear resonance, oxygen coverage can be measured with ML accuracy before and after processin, via SIMNRA simulations, correlating oxygen coverage to data within 1%.

Boron-doped p-Si(100) is found to be always hydrophilic pre-etch, with a γ^T of 53 ± 1.4 mJ/m². After an aqueous HF (1:20) etch, γ^T decreases 10% to 48 ± 2.6 mJ/m², and Si is hydrophobic. GaAs(100) is initially always very hydrophobic with a γ^T of 37 ± 2.0 mJ/m². After etching, Te-doped n+GaAs always becomes hydrophilic with a γ^T increase of 50% to 66 mJ/m² ± 1.4 mJ/m². Native oxides on B-doped p-Si(100) wafers are found by IBA to contain 13.3×10^{15} at/cm² or 13.3 ± 0.3 oxygen monolayers (ML). After an aqueous HF (1:20) etch, Si(100) exhibits only a $11.6 \pm 3\%$ reduction in oxygen to 11.8 ± 0.4 ML. GaAs native oxides contain 7.2 ± 1.4 oxygen ML. After a proprietary passivation-based etch, GaAs native oxides are reduced $49.1 \pm 4\%$ to 3.6 ± 0.2 oxygen ML without change in GaAs surface stoichiometry.

3LCAA can quantify accurately the reactivity of a surface before Nano-Bonding™, which can be correlated to oxygen coverage and structure. High-resolution IBA and 3LCAA allows for a quantitative analysis of Si and GaAs surfaces energies as function of surface processing, enabling for the engineer interactions between surfaces for NanoBonding.

1. Herbots N. *et al.* US Pat. N° 9,018,077 (2015), US Pat. N° 9,018,077 (2017)
2. Herbots N., Islam R., US Pat. Pending (2018), filed March 18, 2018

Bold page numbers indicate presenter

— A —

Abraha, P.: SE+PS-TuM1, **7**
 Abrahami, S.T.: SE+NS+TF-MoM1, **1**
 Abudayyeh, O.K.: SE-TuA3, **12**
 Afshar, A.: SE-TuA4, **12**
 Agnew, L.: SE-TuP7, **14**
 Aimez, V.: PS+EM+SE-TuM2, **5**
 Aksyuk, V.A.: NS+2D+AN+MN+MP+SE-WeM2, **16**
 Aleman, A.: SE+NS+TF-MoM3, **1**; SE-MoA3, **3**
 Alsharif, N.: NS+2D+AN+MN+MP+SE-WeM12, **17**
 Ambat, R.: SE+NS+TF-MoM1, **1**
 Anders, A.: SE+PS-TuM12, **8**; SE+PS-TuM6, **8**
 Aouadi, S.M.: SE-MoA10, **4**
 Arias, P.: SE+NS+TF-MoM3, **1**
 Ark, F.J.: AS+SE-ThM13, **24**
 Arlinghaus, H.: AS+SE-WeA1, **20**
 Armini, S.: SE+PS-TuM3, **7**
 Artuyshkova, K.: AS+SE-WeA11, **21**
 Atanassov, P.: AS+SE-WeA11, **21**
 — B —
 Baik, S.J.: PS+PB+SE-TuA2, **10**
 Barnola, S.: PS+EM+SE-TuM1, **5**; PS+EM+SE-TuM12, **6**
 Bartosik, M.: SE+NS+TF-MoM6, **1**
 Bechu, S.: AS+SE-ThM3, **22**
 Bendikov, T.: AS+SE-ThM4, **22**
 Benjamin, E.: NS+2D+AN+MN+MP+SE-WeM6, **16**
 Bertram, M.E.: AS+SE-ThM13, **24**
 Bielefeld, J.D.: SE-TuP3, **14**
 Billard, A.: SE-TuA9, **13**
 Biolsi, P.: PS+EM+SE-TuM5, **6**
 Boixaderas, C.: PS+EM+SE-TuM12, **6**
 Bonova, L.: PS+PB+SE-TuA9, **11**
 Boris, D.R.: PS+PB+SE-TuA1, **10**; PS+PB+SE-TuA7, **10**
 Brohan, L.: AS+SE-ThM3, **22**
 Brown, K.A.: NS+2D+AN+MN+MP+SE-WeM12, **17**
 Bruggeman, P.J.: PS+AS+EL+EM+SE-WeM12, **19**
 — C —
 Campo, A.: PS+EM+SE-TuM1, **5**
 Canvel, Y.: PS+EM+SE-TuM12, **6**
 Capuano, C.: AS+SE-WeA11, **21**
 Carr, D.M.: AS+SE-ThM11, **23**
 Caruso, A.N.: SE-TuP3, **14**
 Chaudhuri, S.: PS+PB+SE-TuA9, **11**
 Chen, J.K.: SE-MoA5, **3**
 Chen, M.: SE-MoA3, **3**
 Chu, J.P.: SE-MoA5, **3**
 Ciacotich, N.: SE-MoA9, **4**
 Coimbatore Balram, K.: NS+2D+AN+MN+MP+SE-WeM3, **16**
 Cordill, M.J.: SE+NS+TF-MoM4, **1**
 Cornejo, C.E.: AS+SE-ThM13, **24**
 Creus, J.: SE-TuA9, **13**
 Cronin, S.B.: PS+PB+SE-TuA4, **10**
 Culbertson, R.J.: AS+SE-ThM13, **24**
 Cullen, P.J.: PS+PB+SE-TuA10, **11**
 — D —
 Dahotre, N.B.: SE-MoA10, **4**
 Danilovic, N.: AS+SE-WeA11, **21**
 Darnon, M.: PS+EM+SE-TuM2, **5**
 Day, J.M.: AS+SE-ThM13, **24**
 De Alba, R.: NS+2D+AN+MN+MP+SE-WeM2, **16**; NS+2D+AN+MN+MP+SE-WeM5, **16**
 de Kok, J.M.M.: SE+NS+TF-MoM1, **1**
 de Lafontaine, M.: PS+EM+SE-TuM2, **5**
 Dedoncker, R.: SE+NS+TF-MoM4, **1**
 DeJarld, M.T.: PS+AS+EL+EM+SE-WeM3, **17**
 Deluna, M.M.: SE-TuP2, **14**

Depla, D.J.M.G.: SE+NS+TF-MoM4, **1**; SE+PS-TuM10, **8**
 Devaraj, A.: SE-TuA7, **12**
 Dianat, G.: SE-TuP2, **14**
 Diaz, T.C.: AS+SE-ThM13, **24**
 Dick, N.: NS+2D+AN+MN+MP+SE-WeM2, **16**
 Dimond, T.: AS+SE-ThM5, **22**
 Dorsett, L.: SE-TuP3, **14**
 Drnovšek, A.: SE-TuA11, **13**
 Druce, J.W.: AS+SE-ThM1, **22**
 — E —
 Ellsworth, A.A.: AS+SE-ThM11, **23**
 Erdemir, A.: SE-TuA1, **12**
 Eryilmaz, O.L.: SE-TuA1, **12**
 Euchner, H.: SE+NS+TF-MoM6, **1**
 — F —
 Fafard, S.: PS+EM+SE-TuM2, **5**
 Fahey, A.J.: AS+SE-ThM5, **22**
 Fairley, N.: AS+SE-ThM3, **22**
 Farrokhpanah, A.: PS+PB+SE-TuA9, **11**
 Fernandez, V.: AS+SE-ThM3, **22**
 Fisher, G.L.: AS+SE-ThM11, **23**
 Fitz-Gerald, J.M.: SE-TuP7, **14**
 Foley, B.M.: PS+PB+SE-TuA7, **10**
 Franz, R.: SE+NS+TF-MoM4, **1**; SE+PS-TuM6, **8**; SE-TuA11, **13**
 — G —
 Gaskill, D.K.: PS+AS+EL+EM+SE-WeM3, **17**
 Gay, G.: PS+EM+SE-TuM2, **5**
 Gelb, L.D.: AS+SE-ThM12, **23**
 Gillen, G.J.: AS+SE-ThM10, **23**
 Giri, A.: PS+PB+SE-TuA7, **10**
 Goorsky, M.S.: SE+NS+TF-MoM3, **1**
 Gram, L.: SE-MoA9, **4**
 Greczynski, G.: SE+PS-TuM5, **8**; SE-MoA4, **3**
 Greene, J.E.: SE+PS-TuM5, **8**
 Grutzik, S.: NS+2D+AN+MN+MP+SE-WeM2, **16**
 Gu, J.J.: SE-MoA10, **4**
 Gudla, V.C.: SE+NS+TF-MoM1, **1**
 Gulan, M.: PS+PB+SE-TuA10, **11**
 Gundersen, M.: PS+PB+SE-TuA4, **10**
 Gupta, M.: SE-TuP2, **14**
 — H —
 Hahn, R.: SE+NS+TF-MoM6, **1**
 HaLevy, O.: NS+2D+AN+MN+MP+SE-WeM6, **16**
 Han, S.M.: SE-TuA3, **12**
 Hans, M.: SE-MoA4, **3**
 Hartmann, J.M.: PS+EM+SE-TuM1, **5**
 Hauffman, T.: SE+NS+TF-MoM1, **1**
 Havercroft, N.J.: AS+SE-WeA1, **20**
 Hedlund, J.K.: AS+SE-ThM12, **23**
 Hellgren, N.: SE+PS-TuM5, **8**
 Herbots, N.: AS+SE-ThM13, **24**
 Hill, S.: SE-TuA4, **12**
 Hinkle, C.L.: PS+AS+EL+EM+SE-WeM4, **18**
 Ho, Y.-S.: SE-MoA10, **4**
 Hofmann, T.: PS+AS+EL+EM+SE-WeM2, **17**
 Holec, D.: SE+NS+TF-MoM6, **1**; SE+PS-TuM6, **8**
 Holland, G.: NS+2D+AN+MN+MP+SE-WeM5, **16**
 Hopkins, P.E.: PS+PB+SE-TuA7, **10**
 Hopwood, J.: PS+PB+SE-TuA11, **11**
 Hori, M.: PS+EM+SE-TuM13, **7**
 Hosemann, P.: SE-TuA11, **13**
 Hrebik, J.: SE+PS-TuM13, **9**
 Hsieh, J.H.: SE-MoA8, **4**
 Hsu, C.C.: SE-MoA8, **4**
 Huang, S.: PS+EM+SE-TuM4, **5**
 Hultman, L.: SE+PS-TuM5, **8**; SE-MoA4, **3**
 Hung, T.Y.: SE-MoA10, **4**
 Hurard, C.: PS+EM+SE-TuM4, **5**

— I —

Ilic, B.R.: NS+2D+AN+MN+MP+SE-WeM2, **16**; NS+2D+AN+MN+MP+SE-WeM5, **16**
 Ishikawa, K.: PS+EM+SE-TuM13, **7**
 Islam, R.: AS+SE-ThM13, **24**
 — J —
 Jain, V.: AS+SE-ThM6, **23**
 Jang, J.: PS+PB+SE-TuA2, **10**
 Jaouad, A.: PS+EM+SE-TuM2, **5**
 Jarvis, K.L.: SE-TuP5, **14**
 Jeckell, Z.K.: PS+PB+SE-TuA9, **11**
 Jiang, Z.T.: SE+NS+TF-MoM5, **1**; SE+PS-TuM4, **8**
 Johnson, M.J.: PS+PB+SE-TuA1, **10**; PS+PB+SE-TuA7, **10**
 Joshi, S.S.: SE-MoA10, **4**
 Joshi, V.: SE-TuA7, **12**
 — K —
 Kambham, A.: PS+AS+EL+EM+SE-WeM6, **18**
 Kaneko, T.: PS+EM+SE-TuM10, **6**
 Kato, T.: PS+EM+SE-TuM10, **6**
 Kavanagh, K.L.: AS+SE-ThM13, **24**
 Kawasaki, J.: PS+AS+EL+EM+SE-WeM5, **18**
 Kayser, S.: AS+SE-WeA1, **20**
 Kenny, J.: PS+EM+SE-TuM3, **5**
 Kessler, Y.: NS+2D+AN+MN+MP+SE-WeM6, **16**
 Kilner, J.A.: AS+SE-ThM1, **22**
 Kim, H.: PS+PB+SE-TuA11, **11**
 Kim, J.: PS+AS+EL+EM+SE-WeM3, **17**
 Kim, Y.: PS+AS+EL+EM+SE-WeM3, **17**
 Kindlund, H.: SE+NS+TF-MoM8, **2**
 King, S.W.: SE-TuP3, **14**
 Ko, W.: PS+EM+SE-TuM4, **5**
 Kodambaka, S.: SE+NS+TF-MoM3, **1**; SE-MoA3, **3**
 Kolozsvári, S.: SE-TuA11, **13**
 Kondo, H.: PS+EM+SE-TuM13, **7**
 Kragh, K.N.: SE-MoA9, **4**
 Krakover, N.: NS+2D+AN+MN+MP+SE-WeM6, **16**
 Krogstad, D.V.: PS+PB+SE-TuA9, **11**
 Krogstad, E.: AS+SE-WeA9, **21**
 Krylov, S.: NS+2D+AN+MN+MP+SE-WeM2, **16**; NS+2D+AN+MN+MP+SE-WeM5, **16**; NS+2D+AN+MN+MP+SE-WeM6, **16**
 Kumah, D.P.: PS+AS+EL+EM+SE-WeM10, **18**
 Kushner, M.J.: PS+EM+SE-TuM4, **5**; PS+EM+SE-TuM6, **6**
 — L —
 Lagrasta, S.: PS+EM+SE-TuM12, **6**
 Laroussi, M.: PS+PB+SE-TuA12, **12**
 Lee, J.: SE-TuP4, **14**
 Lei, M.K.: SE+NS+TF-MoM5, **1**; SE+PS-TuM4, **8**; SE-TuA8, **13**
 Li, C.: SE-MoA8, **4**
 Li, L.: NS+2D+AN+MN+MP+SE-WeM12, **17**
 Li, Y.G.: SE+NS+TF-MoM5, **1**; SE-TuA8, **13**
 Liao, M.E.: SE+NS+TF-MoM3, **1**
 Lin, J.: SE-TuA12, **13**
 Lin, Y.: SE-TuP4, **14**
 Linford, M.R.: AS+SE-ThM6, **23**
 Liu, T.: PS+PB+SE-TuA3, **10**
 Liu, Y.Y.: SE-MoA10, **4**
 Loup, V.: PS+EM+SE-TuM1, **5**
 Lu, J.: SE-MoA4, **3**
 — M —
 Mahoney, C.: AS+SE-WeA2, **20**
 Malik, S.: SE-TuP3, **14**
 Mangus, M.: AS+SE-ThM13, **24**
 Marcoen, K.: SE+NS+TF-MoM1, **1**
 Marina, O.A.: SE-TuA7, **12**
 Martinez, A.: SE-TuA7, **12**
 Martinez, E.: PS+EM+SE-TuM12, **6**

Author Index

- Martinu,: SE-MoA1, **3**
 Mayrhofer, P.H.: SE+NS+TF-MoM6, **1**
 McArthur, S.L.: SE-TuP5, **14**
 Melia, M.A.: SE-TuP7, **14**
 Meng, D.: SE-TuA8, **13**
 Merche, D.: PS+PB+SE-TuA8, **11**
 Merrill, D.: SE-TuP3, **14**
 Mihut, D.: SE-TuA4, **12**
 Milosavljević, V.: PS+PB+SE-TuA10, **11**
 Moellers, R.: AS+SE-WeA1, **20**
 Mohades, M.: PS+EM+SE-TuM6, **6**
 Mol, J.M.C.: SE+NS+TF-MoM1, **1**
 Møller, P.: SE-MoA9, **4**
 Moraes, V.: SE+NS+TF-MoM6, **1**
 Mosden, A.: PS+EM+SE-TuM6, **6**
 Mraz, S.: SE-MoA4, **3**
 Muench, F.: AS+SE-ThM4, **22**
 Munigetj, R.: AS+SE-WeA7, **20**
 Muramoto, S.: AS+SE-ThM10, **23**
 Murugesan, V.: SE-TuA7, **12**
 Myers-Ward, R.L.: PS+AS+EL+EM+SE-WeM3, **17**
 — N —
 Nam, S.: PS+EM+SE-TuM4, **5**
 Narayan, S.R.: AS+SE-ThM13, **24**
 Nelson, C.M.: SE-TuA3, **12**
 Nie, X.: SE+PS-TuM2, **7**
 Niehuis, E.: AS+SE-WeA1, **20**
 — O —
 Oh, H.-J.: PS+PB+SE-TuA2, **10**
 Ohya, Y.: PS+EM+SE-TuM13, **7**
 Orłowski, J.: AS+SE-WeA7, **20**
 Ozkan, A.: PS+PB+SE-TuA8, **11**
 — P —
 Pacholski, M.L.: AS+SE-WeA8, **20**
 Pachuta, S.J.: AS+SE-WeA3, **20**
 Palisaitis, J.P.: SE+PS-TuM5, **8**
 Pan, N.: SE+NS+TF-MoM5, **1**
 Panjan, M.: PS+AS+EL+EM+SE-WeM11, **18**
 Paquette, M.M.: SE-TuP3, **14**
 Pargon, E.: PS+EM+SE-TuM2, **5**
 Pavunny, S.P.: PS+AS+EL+EM+SE-WeM3, **17**
 Persson, P.O.A.: SE+PS-TuM5, **8**
 Petit-Etienne, C.: PS+EM+SE-TuM2, **5**
 Petrov, I.: SE+PS-TuM5, **8**
 Petrova, L.: PS+PB+SE-TuA1, **10**
 Petrova, Tz.B.: PS+PB+SE-TuA7, **10**
 Pirkl, A.: AS+SE-WeA1, **20**
 Po, G.: SE-MoA3, **3**
 Poirier, D.M.: AS+SE-WeA3, **20**
 Posseme, N.: PS+EM+SE-TuM1, **5**
 — Q —
 Qiao, K.: PS+AS+EL+EM+SE-WeM3, **17**
 — R —
 Rachidi, S.: PS+EM+SE-TuM1, **5**
 Rading, D.: AS+SE-WeA1, **20**
 Ram, S.: AS+SE-ThM13, **24**
 Ramirez, G.: SE-TuA1, **12**
 Rand, R.H.: NS+2D+AN+MN+MP+SE-WeM2, **16**
 Ranjan, A.: PS+EM+SE-TuM5, **6**
 Rasmussen, J.B.: SE-MoA9, **4**
 Rauf, S.: PS+EM+SE-TuM3, **5**
 Razavi, H.: PS+PB+SE-TuA12, **12**
 Rebelo de Figueiredo, M.: SE-TuA11, **13**
 Reniers, F.: PS+PB+SE-TuA8, **11**
 Rhodes, K.: AS+SE-WeA7, **20**
 Richard-Plouet, M.: AS+SE-ThM3, **22**
 Riedl, H.: SE+NS+TF-MoM6, **1**
 Rodrigues, W.N.: AS+SE-ThM11, **23**
 Rosen, J.: SE+PS-TuM5, **8**
 Rubinstein, I.: AS+SE-ThM4, **22**
 Ruzic, D.N.: PS+PB+SE-TuA9, **11**
 — S —
 Sadighi, S.: PS+EM+SE-TuM3, **5**
 Sanchette, F.: SE-TuA9, **13**
 Sangiovanni, D.G.: SE-MoA3, **3**
 Sankaran, R.M.: PS+PB+SE-TuA3, **10**
 Sarafian, A.R.: AS+SE-ThM5, **22**
 Scally, L.: PS+PB+SE-TuA10, **11**
 Schmidt, B.W.: AS+SE-ThM11, **23**
 Schneider, J.M.: SE-MoA4, **3**
 Schroeder, C.: PS+PB+SE-TuA4, **10**
 Schroeder, W.: PS+PB+SE-TuA4, **10**
 Scully, J.R.: SE-TuP7, **14**
 Seidel, S.: SE-TuP2, **14**
 Sekine, M.: PS+EM+SE-TuM13, **7**
 Serov, A.: AS+SE-WeA11, **21**
 Shen, S.: AS+SE-WeA9, **21**
 Shen, Y.: SE-TuA3, **12**
 Shim, S.: PS+EM+SE-TuM4, **5**
 Shutthanandan, V.: SE-TuA7, **12**
 Singleton, D.: PS+PB+SE-TuA4, **10**
 Sisco, E.: AS+SE-ThM10, **23**
 Skelton, J.M.: SE-TuP7, **14**
 Sortica, M.: SE+PS-TuM5, **8**
 Sridhar, S.: PS+EM+SE-TuM5, **6**
 Staykov, A.: AS+SE-ThM1, **22**
 Stevens, E.: SE-TuA7, **12**
 Stoyanov, P.: SE-TuP6, **14**
 Strohmeier, B.: AS+SE-WeA7, **20**
 Subramanian, S.: PS+PB+SE-TuA4, **10**
 Sushko, P.V.: SE-TuA7, **12**
 Susman, M.D.: AS+SE-ThM4, **22**
 — T —
 Tanaka, K.: SE+NS+TF-MoM3, **1**
 Tellez, H.: AS+SE-ThM1, **22**
 Terryn, H.: SE+NS+TF-MoM1, **1**
 Thapa, R.: SE-TuP3, **14**
 Thevuthasan, S.: SE-TuA7, **12**
 Thörnberg, J.: SE+PS-TuM5, **8**
 Tian, W.: PS+EM+SE-TuM3, **5**
 Tomko, J.: PS+PB+SE-TuA7, **10**
 Tsutsumi, T.: PS+EM+SE-TuM13, **7**
 — U —
 Ueyama, T.: PS+EM+SE-TuM13, **7**
 — V —
 Valeriano, W.W.: AS+SE-ThM11, **23**
 Vaskevich, A.: AS+SE-ThM4, **22**
 Verkouteren, J.: AS+SE-ThM10, **23**
 Vlasak, P.R.: AS+SE-WeA8, **20**
 Vo, H.: SE-TuA11, **13**
 Volatier, M.: PS+EM+SE-TuM2, **5**
 Voronin, S.A.: PS+EM+SE-TuM5, **6**
 — W —
 Wagner, S.: SE-TuP3, **14**
 Walker, A.V.: AS+SE-ThM12, **23**
 Wallin, C.B.: NS+2D+AN+MN+MP+SE-WeM2, **16**; NS+2D+AN+MN+MP+SE-WeM5, **16**
 Walton, S.G.: PS+PB+SE-TuA1, **10**; PS+PB+SE-TuA7, **10**
 Wang, J.-C.: PS+EM+SE-TuM3, **5**
 Wang, M.: PS+EM+SE-TuM6, **6**
 Wang, Y.: SE+NS+TF-MoM3, **1**
 Wei, B.W.: SE-MoA10, **4**
 Westly, D.A.: NS+2D+AN+MN+MP+SE-WeM2, **16**
 Wheeler, J.M.: SE-MoA3, **3**
 Wu, G.: SE-TuP4, **14**
 — X —
 Xia, A.: SE+NS+TF-MoM4, **1**; SE-TuA11, **13**
 — Y —
 Yamaguchi, H.: NS+2D+AN+MN+MP+SE-WeM10, **17**
 Yang, S.: PS+PB+SE-TuA4, **10**
 Yao, J.: AS+SE-WeA9, **21**
 Yu, C.C.: SE-MoA5, **3**
 Yu, X.-Y.: AS+SE-WeA9, **21**
 Yuan, H.: SE+NS+TF-MoM5, **1**
 — Z —
 Zaid, H.: SE+NS+TF-MoM3, **1**; SE-MoA3, **3**
 Zakel, J.: AS+SE-WeA1, **20**
 Zehnder, A.T.: NS+2D+AN+MN+MP+SE-WeM2, **16**
 Zha, W.: SE+PS-TuM2, **7**
 Zhao, C.: SE+PS-TuM2, **7**
 Zhirkov, I.: SE+PS-TuM5, **8**
 Zhu, W.: PS+PB+SE-TuA9, **11**
 Zhu, Z.H.: AS+SE-WeA9, **21**
 Zöhrer, S.: SE+PS-TuM6, **8**