Plasma Science and Technology Division
Room: Ballroom B - Session PS+SS-TuA

The Science of Plasmas and Surfaces: Commemorating the Career of Harold Winters (ALL INVITED SESSION)
Moderators: Sumit Agarwal, Colorado School of Mines, Selma Mededovic, Clarkson University

2:20pm **PS+SS-TuA1 History and Legacy of the Coburn and Winters Paper**, ***R.Mohan Sankaran***, Case Western Reserve University, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands

The Coburn and Winters paper[1] is a hallmark contribution in the field of plasma processing. The study revealed very simply and cleverly the role of a plasma in reactive ion etching. When a silicon (Si) surface was exposed to an argon (Ar) ion beam alone or xenon difluoride (XeF_2) alone, the etch rate was found to be negligible. This showed that physical sputtering and chemical etching in the former and latter cases, respectively, could not effectively etch Si. In stark contrast, combining the Ar ion beam and XeF_2 resulted in a significantly higher etch rate, underscoring the synergistic mechanism of fluorine radicals reacting with the Si surface and Ar ions bombarding and kicking them off to ultimately remove Si atoms. The legacy of these experiments is not only the technological impact it has had on applications of plasma processes to semiconductor manufacturing, but, more broadly speaking, the foundation it has laid for plasma science by demonstrating how a complex system can be unraveled to yield simple correlations. This is reflected here every year at AVS where the etching sessions continue to be the largest of all the sessions in the Plasma Science and Technology Division. In this introductory talk to the session commemorating Harold Winters, a history of the Coburns and Winters experiment and its impact on plasma science and technology will be presented.

1. J. W. Coburn and H. F. Winters, *J. Appl. Phys.***50**, 3189 (1979).

2:40pm **PS+SS-TuA2 The Reaction of Fluorine Atoms with Silicon: Controversies 38 Years in the Making**, ***Vincent M. Donnelly***, University of Houston

Chemical etching of silicon by fluorine atoms in the absence of ion bombardment is reviewed. Controversies on the identity of etching products and reaction probabilities are discussed. Attempts are made to explain the apparent presence of SiF_2 as a primary product in many studies, dating back to 1980, but not in others, including those of Harold Winters from as early as 1979. Reported estimates of reaction probabilities (here defined as the probability of removing a Si atom from the substrate per incident F atom) vary by a factor of 2000. When these values, with some corrections and normalizations applied, are plotted as a function of F atom flux, most of them fall on a "universal curve" that reveals a large (~30-fold) decrease in the reaction probability with increasing F flux, from 0.03 at a F flux $10^{12}cm^{-2}s^{-1}$ to 0.001 at a flux of 10^{20} $cm^{-2}s^{-1}$. These values were extracted from beam experiments with F atoms generated from cracking of F_2, including those by Harold Winters, from isotropic etching in plasma experiments (both in-plasma and downstream) with F_2, $CF_4/10\%O_2$, and NF_3 feed gases, as well as from molecular dynamics simulations. Reaction coefficients derived from chemical etching rates in SF_6 plasmas do not follow this trend, however, suggesting a large enhancement in the F reaction probability (~20 to 100-fold at F fluxes of 10^{18}-$10^{19}cm^{-2}s^{-1}$), due to the presence of sulfur.

3:00pm **PS+SS-TuA3 The Long Quest to Understand Etch Mechanisms and Surface Science: The Legacy of Harold Winters and its Impact on Semiconductor Industry**, ***Sebastian Engelmann***, *N.C.M. Fuller*, IBM Research Division, T.J. Watson Research Center

From the beginning of its days in semiconductor industry until now, Harold Winters work has very big impact to plasma processes and surface science. Starting with his landmark papers in the 1970's and 1980's, much scientific work was inspired by his publications. At IBM itself and industry-wide, many projects were impacted by his work. We will present our view on some of these topics as well as the lasting technological impact that Harold's work had and it inspired.

3:20pm **PS+SS-TuA4 Surface Science Aspects of (Plasma) ALD reactions**, *V. Vandalon, M.C.M. van de Sanden*, ***Erwin Kessels***, Eindhoven University of Technology, The Netherlands

The profound contributions of Harald Winters and John Coburn to the field of plasma etching have inspired us at the Eindhoven University of Technology to study the surface-science aspects of plasma deposition. The latter has been an overarching theme within our research in the last two decades. It started with investigations of the growth mechanism of amorphous carbon and silicon films prepared by plasma-enhanced chemical vapor deposition (PECVD) and it resulted even in beam-experiment-type studies using advanced real-time diagnostic probes in a dedicated high vacuum reactor [1]. The interest in understanding the surface reactions during film growth was also the motivation to step into the field of atomic layer deposition (ALD). ALD film growth is truly ruled by surface chemistry and, inspired by work of others, we recognized that the ALD field could greatly benefit from plasma-assisted processes [2]. Like in other cases of (plasma-based) film growth, a detailed understanding of the surface-science aspects is key to take advantage of all opportunities the method provides. This has been the driver for many experimental studies of the film growth by thermal and plasma ALD using a wide variety of gas phase and surface diagnostics [3]. It has also been the trigger to set up nonlinear optical studies of the surface processes during ALD, culminating in advanced broadband sum-frequency generation (SFG) studies [4]. In this contribution, the historical perspective of our research will be sketched and some recent highlights will be presented.

[1] See for example, J.J.H. Gielis *et al*., Phys. Rev. B 77, 205329 (2008).

[2] See the review paper by H.B. Profijt *et al*., J. Vac. Sci. Technol. A. 29, 050801 (2011).

[3] See for example, Heil *et al*., Appl. Phys. Lett. 89, 131505 (2006) and Langereis *et al*., Appl. Phys. Lett. 92, 231904 (2008).

[4] See for example V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. 108, 011607 (2016).

4:20pm **PS+SS-TuA7 Harold Winters and Plasma-Surface Interactions**, ***David Graves***, University of California at Berkeley

My trajectory in studying plasma-surface interactions was profoundly affected first by reading the papers of Harold Winters, then by talking and working with him. My co-workers and I read and re-read Harold's papers (often co-authored with John Coburn) and the insights we gained from this work had a huge impact on what we chose to investigate and how we interpreted our results. In particular, our early studies of plasma-surface interactions using molecular dynamics simulations were almost completely motivated and guided by his work. Later, I had the extraordinary good fortune to welcome Harold into my laboratory for several years as a visiting scholar. His presence (and that of John Coburn and Dave Fraser) enlightened, instructed and inspired my entire group. I will summarize the impact of Harold's scientific work, his gracious and generous personality and his innate enthusiasm for science on me and my research group.

4:40pm **PS+SS-TuA8 Illuminating the Black Box: Plasma-Surface Interactions at the Atomic Scale**, ***Jane Chang***, UCLA

This talk pays tributes to Harold Winters's seminal contributions in the field of plasma etching of silicon-based materials and metals. Inspired by one of the earliest papers of Harold Winters, where he presented a framework for understanding plasma etching by treating the plasma as a "pseudo-black-box" to provide a semi-quantitative understanding of plasma etching effects such as loading, this talk presents a generalized methodology, combining thermodynamic assessment and kinetic verification of surface reactions, to further illuminate the black box in an effort to tailor plasma-surface interactions for a wide range of materials. This talk does not attempt to review all of Harold Winters's work but focus on his work in metal etch and how that foundational knowledge helps guide the fundamental research in these areas to further advancements in tailoring the plasma-surface interactions to achieve desirable etch efficacy and selectivity of metals at the atomic scale.

5:00pm **PS+SS-TuA9 Controlling Low Temperature Plasma Surface Interactions for Atomic Layer Etching of Electronic Materials And Atmospheric Pressure Plasma-Treatments of Model Polymers and Biomolecules**, ***Gottlieb S. Oehrlein***, University of Maryland, College Park

Harold Winters's pioneering work on the scientific understanding of plasma-surface interactions, in particular as applied to low temperature plasma-based etching of materials, much of it done in collaboration with John Coburn, [1] has become textbook material. As a colleague at IBM Research I had the opportunity to learn from Harold by discussing with him ideas on rate limiting factors in etching reactions, in particular the role of surface reaction layers and the role of ion bombardment. These topics were of great interest to him as a possible explanation of ion-neutral synergy and also of the doping effect of silicon etching. In this talk I will discuss the relationship of Harold's work to topics in my own research, in particular to recent work performed by members of my group. These include atomic layer etching of SiO_2 and other materials[2] and interaction of the effluent of atmospheric pressure plasma sources with polymers and biomolecules.[3]

[1] H.F. Winters and J.W. Coburn, "Surface science aspects of etching reactions," Surf. Sci. Rep. 14, 161 (1992)

[2] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, “Fluorocarbon assisted atomic layer etching of SiO_2 using cyclic Ar/ C_4F_8 plasma”, J. Vac. Sci. Technol. A **32**, 020603 (2014).

[3] E. A. J. Bartis, A. J. Knoll, P. Luan, J. Seog, and G. S. Oehrlein, “On the Interaction of Cold Atmospheric Pressure Plasma with Surfaces of Bio-molecules and Model Polymers”, Plasma Chemistry and Plasma Processing **36**, 121 (2016); P. Luan, A. J. Knoll, H. Wang, V. S. S. K. Kondeti, P. J. Bruggeman, and G. S. Oehrlein, "Model polymer etching and surface modification by a time modulated RF plasma jet: role of atomic oxygen and water vapor," Journal of Physics D-Applied Physics **50**, 03LT02 (2017).

* I gratefully acknowledge the contributions and collaboration of D. Metzler, Kang-Yi Lin, C. Li, S. Engelmann, R. Bruce, E. Joseph, E. A. J. Bartis, A. J. Knoll, P. Luan, J. Seog, V. S. S. K. Kondeti, P. J. Bruggeman and D. Graves to some of the topics in this talk. Additionally, funding from National Science Foundation (CBET-1134273, PHY-1004256, PHY-1415353), US Department of Energy (DE-SC0001939) and Semiconductor Research Corporation (No. 2017-NM-2726) is thankfully acknowledged.

5:20pm **PS+SS-TuA10 H-induced Defect Kinetics in a-Si:H: Obtaining Kinetic Parameters from Temperature-Dependent Data**

F.J.J. Peeters, DIFFER, Netherlands, *J. Zheng,* Peking University, China, *I.G.M. Aarts,* ASML, *A.C.R. Pipino,* ONR, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands, ***Richard van de Sanden***, DIFFER, Netherlands

Near-IR Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) has been applied to study the defect evolution in an a-Si:H thin film subjected to a calibrated directed beam of atomic H at different substrate temperatures (80 to 200 °C) . To this end a 42 ± 2 nm a-Si:H film was grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by Hot-Wire Chemical Vapor Deposition (HW-CVD). A fully reversible defect creation process is observed, with a non-linear dependence on H flux, with a time resolution of 33 ms and a relative sensitivity of 10^{-7}. Through the use of polarizing optics the CRDS signal was split into *s*- and *p*-polarized components, which, combined with *E*-field calculations, provides depth sensitivity. Extensive kinetic modeling of the observed process is used to determine rate constants for the hydrogen-material interactions and defect formation in a-Si:H, as well as revealing a high diffusion coefficient for atomic H on the order of 10^{-11} cm^2s^{-1}. A novel reaction pathway is proposed whereby H inserted into weak Si-Si bonds recombines with mobile H, resulting in a limited penetration depth for atomic H from the gas-phase on the order of 15 nm. The defect evolution kinetics can be modeled based on a quasi-steady-state approximation of H atoms, which assumes that the H density in the film reaches a quasi-steady-state very rapidly and exhibits little change with time. This approximation significantly simplifies the kinetic model, accurately predicts the initial absorption change behavior and allows quantitative evaluation of the kinetic parameters of the microscopic processes and the corresponding activation energies.

5:40pm **PS+SS-TuA11 Translating Fundamental Science to Technology Development in Plasma Assisted Materials Processing: Contributions by Harold Winters and Their Impact on Modeling**

Mark Kushner*, C.M. Huard, S.J. Lanham, S. Huang, P. Tian,* University of Michigan

A hallmark of the contributions of Harold Winters to the advancement of plasma materials processing is beginning with fundamental processes, and building upon this foundational knowledge towards technology development. His contributions to our understanding of ion assisted chemical sputtering, adsorption, desorption, chemisorption, conductance in features, stopping distances, mixing layers and electron impact dissociation cross sections are examples of producing foundational knowledge which enabled the work of colleagues in the field. This enabling aspect of his work is nowhere more true than for modeling and simulation, as first principles models begin with these foundational principles. In this talk, key foundational contributions by Harold Winters in plasma-surface interactions and electron impact processes will be reviewed from the perspective of enabling first principles modeling. Examples will be discussed from reactor and feature scale modeling of conductor and dielectric plasma etching, with emphasis on aspect ratio dependent etching and atomic layer etching.

Work was supported by National Science Foundation, Department of Energy Office of Fusion Energy Science, Lam Research and Samsung Electronics.

6:00pm **PS+SS-TuA12 Extending the Legacy of Harold Winters: Probing the Energetics and Plasma-Surface Interface of Halogenated Plasmas**

Ellen Fisher, Colorado State University

In the arena of halocarbon plasma chemistry, Harold Winters and co-workers performed pioneering work by extensively exploring plasma-assisted etching of semiconductor materials using a range of halogenated systems. For example, Coburn and Winters explored the role of energetic ions in plasma-assisted etching in silicon-fluorine systems, studying the dynamic interplay between physical and chemical sputtering. This work has inspired several decades of work on halogenated plasma systems, including further elucidation of the role of ions and other energetic species within plasmas. In this work, energy partitioning for molecules formed from fluorinated plasma systems has been measured using laser-induced fluorescence, optical emission and broadband absorption spectroscopies. Focusing on two fluorinated species, SiF in SiF_4 plasmas and CF_x in C_xF_y fluorocarbon plasmas, we find that small molecules in these systems exhibit extremely high electronic excited state vibrational temperatures, T_V, relative to rotational temperatures, T_R. This suggests that vibrational modes are preferentially excited over other degrees of freedom. Using the imaging of radicals interacting with surfaces (IRIS) technique, surface scattering coefficients measured for each radical show a strong correlation with the associated T_V, with little dependence upon $T_R$or translational temperatures. This presentation will focus on plasma deposition and etching systems where understanding the relationship between the gas-phase and the resulting surface properties allows for deeper insight into creating advanced functional materials for a range of applications. Specific examples will include fluorocarbon film formation as well as production and modification of multidimensional materials.

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