Unraveling atomic-level self-organization at the plasma-material interface

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The intrinsic dynamic interactions at the plasma-material interface and critical role of irradiation-driven mechanisms at the atomic scale during exposure to energetic particles require *a priori* the use of *in-situ* surface characterization techniques [1]. Characterization of "active" surfaces during modification at atomic-scale levels is becoming more important as advances in processing modalities are limited by an understanding of the behavior of these surfaces under realistic environmental conditions. Self-organization from exposure to non-equilibrium and thermalized plasmas enable dramatic control of surface morphology, topography, composition, chemistry and structure yielding the ability to tune material properties with an unprecedented level of control. Deciphering self-organization mechanisms of nanoscale morphology (e.g. nanodots, ripples) and composition on a variety of materials including: compound semiconductors, semiconductors, ceramics, polymers and polycrystalline metals via low-energy ion-beam assisted plasma irradiation are critical to manipulate functionality in nanostructured systems.

By operating at ultra-low energies near the damage threshold, irradiation-driven defect engineering can be optimized and surface-driven mechanisms controlled. Tunability of optical, electronic, magnetic and bioactive properties is realized by reaching metastable phases controlled by atomic-scale irradiation-driven mechanisms elucidated by novel *in-situ* diagnosis coupled to atomistic-level computational tools. In this work we present data *in-operando* the mechanisms responsible for low-energy (250-1000 eV) Ar, Kr and Ne irradiation of III-V semiconductors and Si nanopatterning. We conduct measurements of surface composition and chemistry with environmental XPS and low-energy ion spectroscopy (LEISS) illustrating the importance of *in-operando* and *in-situ* characterization of the surface and sub-surface regions from first ML down to about 10-nm. High-pressure low-energy ion scattering spectroscopy and mass spectrometry are also combined to elucidate mass redistribution and ion-induced desorption mechanisms at play during nanostructuring. Additional examples including ZnO nanoparticles on PDMS and nanopatterning of 70-nm $TiO2$ thin films on biosensors are presented to illustrate *in-situ* PMI techniques.

[1] J.P. Allain and A. Shetty, J. Phys. D: Appl. Phys, 50 (2017) 283002, *Invited Topical Review*

Supplementary Page

The *in-situ in-operando* facility known as IGNIS (Ion-Gas-Neutral Interaction with Surfaces) facility at the University of Illinois at Urbana-Champaign led by Prof. Allain's group. The facility provides a unique suite of surface-sensitive characterization *during multi-particle irradiation exposure (e.g. low-temperature plasmas, low-energy ions and atoms)* to drive dissipative structure formation enabling measurement of both composition and morphology simultaneously. On the right, an illustration of the conceptual approach for directed irradiation synthesis of surface structures balancing stimulus rate (e.g. multi-particle incident flux) and material response rate (e.g. dissimilar material combinations such as metal oxides and polymers). The talk will highlight a few examples (e.g. nanopatterning of III-V and Si semiconductors and others) to demonstrate how *in-situ in-operando* characterization of the surface (first ML by LEISS and direct recoil spectroscopy) and sub-surface with XPS can help guide nanopatterning synthesis.

The approach proposed here is to establish a first-principles understanding of the materials response rate to the modifying or stimulus processing parameters (e.g. temperature, particle energy, flux) and enable the rational design of advanced materials using scalable manufacturing technologies (i.e. to high-value manufacturing) during the discovery phase of novel multi-functional and multi-scale materials. In particular, IGNIS has also been very important to study multi-component surfaces and dissimilar materials. Some additional dissimilar material platforms: *1) soft combined with hard materials (e.g. high vs low material response rates, respectively) using metal-oxides combined with soft polymeric substrates: ZnO with PDMS 2) Au or Ag nanoparticle synthesis during irradiation with soft hydrogels and 3) TiO2 thin-films used as biosensors with photonic crystals.*

The main purpose of the talk will be to highlight the advantages of capturing real-time evolution of the top surface under high-pressure (e.g. mtorr) conditions with LEISS and XPS for enhanced control of nanopatterning and nanostructure synthesis.