White Paper for *Frontiers of Plasma Science Panel*

Date of Submission:	19 June 2015

Indicate the primary area this white paper addresses by placing "P" in right column.
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	"P", "S"
• Plasma Atomic physics and the interface with chemistry and biology	P
• Turbulence and transport	
• Interactions of plasmas and waves	
• Plasma self-organization	
• Statistical mechanics of plasmas	

Indicate type of presentation desired at Town Hall Meeting.

	"X"
Oral	
Poster	
Either Oral or Poster	X
Will not attend	Cannot attend 2nd day

Title:	**Plasma-Surface Interactions in Ultra-Low Te Plasmas**
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1. Research frontier and importance of the scientific challenge

One of the most important technological uses of low temperature plasmas is in the synthesis and modification of materials. Indeed, the mix of charged particles (electrons and ions), reactive gas molecules and atoms, and excited species produces a flux of charged and reactive neutral particles as well as photons at a material surface that has been adventitiously applied to the modification of materials, ranging from surface functionalization to thin film growth and etching. However, with the rapidly evolving demand for monolayer materials and single nanometer-scale precision, there is a rising interest in minimizing and finely controlling the kinetic energy of ions as they impact surfaces. Generally, ion energies should be large enough to stimulate surface reactions but low enough to prevent damage. Unfortunately, exact values for a given material system are unknown, largely because *there is limited understanding of the response of materials exposed to plasmas that deliver a flux ions with kinetic energies below about 20 eV*.

There are two unique aspect of energy delivery to a surface exposed to plasmas, particularly as it applies processing plasmas. The first is the synergistic effect associated with the simultaneous delivery of reactive

neutrals, photons, and energetic ions. It is well-known [Coburn] that the material response is minimal (or nill) when only exposed to one of the constituents. The second is the non-equilibrium nature of energy delivery. That is, the energy delivered by particles or photons produces a well-localized "thermal spike" that exceeds the average temperature of the material.[1] To understand this, consider that particles can deliver both kinetic energy and potential energy to the surface, where it is typically absorbed in the first few monolayers of the material, depending on the velocity of the incoming particle. Photons on the other hand, can penetrate much deeper before losing their energy. Nonetheless, the energy is deposited in close proximity to the point of contact. For highly energetic ions, the local effects can be dramatic, including defect generation and material ejection (sputtering or etching). However, it remains unclear what happens when the kinetic energy is low. Consider the case where ion kinetic energies are no more than a few eV (at or below the bond strength of most materials). Here, it is reasonable to assume the potential energy released during neutralization contributes to the aforementioned thermal spike but, isn't it equally reasonable to assume any effect is negligible if the fluence is small? And, to what extent is the response material dependent? Importantly, does the mechanism by which ion energy is delivered, strongly alter or diminish the interplay between reactive species, photons, and ions at the surface?

Beyond the materials processing implications, the interactions of plasmas delivering a flux of low kinetic energy or even thermal ions to surfaces are relevant to cold plasmas found in space environments and a variety of applications that employ atmospheric pressure plasmas.

2. Scientific approach to advancing the frontier and indicate if new research tools or capabilities are required

Advancing our understanding of the interaction between very low kinetic energy ions and materials during plasma exposure requires new lines of inquiry in both experiment and theory. This includes extending existing techniques and developing new approaches in the areas outlined below.

Ultra low electron temperature plasmas. Sources characterized by electron temperatures below 1 eV are needed to ensure ion kinetic energies are low as they impact adjacent surfaces. Existing sources such as electron beam driven plasmas [2] and flowing afterglow plasmas [3] can be used to generate plasmas with electron temperatures that are well below 1 eV at the plasma-surface interface. Magnetically confined or high pressure sources may also meet the criteria.

Low energy ion beams. Experiments employing low energy ion beams can certainly be used to better understand basic processes. There are numerous studies, extending back several decades using beams comprised of noble gas ions, with energies extending down to typical sputter/etch thresholds (20-30 eV). However, experiments using ion beams with energies in the sub 10 eV range, with narrow distributions and variable current densities are largely absent. This is not particularly surprising, since ion guns of this variety are not easy to build.

Real-time monitoring of the surface. Plasma-driven surface reactions are often developed using post treatment, *ex situ* surface diagnostics to "re-construct" surface reactions that can lead to changes in surface properties. However, much could be learned by monitoring the surface during plasma exposure. To this end, existing or new *in situ*, real-time surface diagnostic combined with plasma diagnostics and simulations to monitor and understand the response of surfaces exposed to low T_e plasmas will be needed.

Theory/Modeling. Interest in the interaction of low kinetic energy ions with surfaces has a long history. In the 1950's, Homer Hagstrum developed the basic concept of ion-induced potential electron emission, [4] which laid the groundwork for understanding the importance of ion charge. Much of the work, however, considers only ion-surface interactions and was typically benchmarked against surface science experiments conducted under ultra-high vacuum conditions using noble gas ions. Modern plasmas simulations using molecular dynamics approaches often treat the incoming ions as fast neutrals, a reasonable approximation if the kinetic energy is much higher than the ionization potential. To address the need for very low kinetic ions, one should consider both the kinetic and potential energies.

3. Impact of this research on plasma science and related disciplines and potential for societal benefits:

Plasma processing plays a role in the fabrication of many commonplace devices, materials, and components used in military systems as well as the general public. Etching, deposition, cleaning, and other fabrication steps are performed in plasma tools to produce products ranging from electronic devices to high-end glass and metal products, photovoltaic devices and sensors. The ongoing evolution of technology toward nanoscale precision requires new approaches to plasma processing, which combine low gas pressure, high ion density, low plasma potential, and chemistries which are capable of anisotropic ion bombardment at low, controlled energies. Here, ultra-low T_e plasmas and their ability to deliver very low energy ions meet the need. Clearly then, a better understanding of the role of these ions will not only advance the associated science and technology, it has the potential to broadly impact and advance technology used across all of society.

References

1. A. Anders, "A structure zone diagram including plasma-based deposition and ion etching," Thin Solid Films 518, 4087 (2010).
2. S. G. Walton, D. R. Boris, S. C. Hernández, E. H. Lock, Tz. B. Petrova, G. M. Petrov, and R. F. Fernsler, "Electron Beam Generated Plasmas for Ultra Low Te Processing," ECS J. Solid State Sci. Technol. 4 N5033 (2015).
3. G. J. Meeusen, E. A. Ershov-Pavlov, R. F. G. Meulenbroeks, M. C. M. van de Sanden, and D. C. Schram, "Emission spectroscopy on a supersonically expanding argon/silane plasma," J. Appl. Phys. 71, 4156 (1992)
4. H. D. Hagstrum, "Theory of Auger Ejection of Electrons from Metals by Ions," Phys. Rev. 96, 336 (1955).

Figure

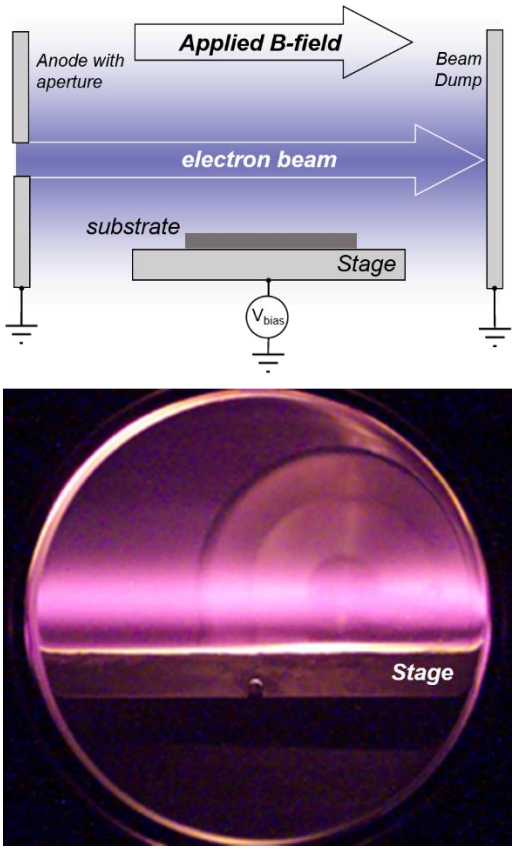

Figure 1 – The US Naval Research Laboratory's Large Area Plasma Processing System (LAPPS) employs an electron beam generated plasmas for use in materials processing applications. (Top) Simplified schematic of the system and (Bottom) an image of the plasma through a 6" port.