

# Laser-Collision Induced Fluorescence in Highly Collisional Helium Discharges

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Development and implementation of plasma diagnostics has been and continues to be a central thrust necessary to advance our understanding of plasma discharges. This is of particular importance for plasmas generated near and beyond atmospheric pressures as high degrees of collisionality significantly reduce the lifetime of excited states often used as a basis for interrogation.

To further the develop of the laser-collision induced fluorescence (LCIF) method [1], [2] for use in such plasmas, a 400 Torr helium discharge, in a point-to-point configuration (Fig. 1a) is being studied. The filament is initially generated by a 200 ns high voltage pulse and is then subsequently driven by a second “heating” voltage pulse (1  $\mu$ s duration, 1.5  $\mu$ s after initial plasma generation) to induce the plasma into a desired E/N. A key and potentially transformative element of the ongoing effort is the utilization of short pulse ( $\sim$ 100 fs) laser to initiate the LCIF process (see Fig. 1a). For the data presented here, LCIF is observed for 10 ns, starting  $\approx$ 1 ns before laser excitation. Preliminary trends in the LCIF generated by short-pulse excitation of a 400 Torr helium discharge are presented in Fig. 1b as functions of E/N (electric field/gas number density, 1 Td =  $10^{-17}$  V-cm<sup>2</sup>) with a nominally fixed electron density of  $\approx$  $2 \times 10^{13}$  cm<sup>-3</sup>. As neither the neutral density nor neutral temperature likely changed over most of the surveyed E/N, the trends demonstrates that the increasingly energetic electrons contribute to a significant component of the observed LCIF.

The work presented here constitutes a proof-of-principle demonstration that LCIF can be used to measure fundamental electron properties (density and temperature) under near-atmospheric conditions. The work also demonstrates that short-pulse laser excitation can be used to interrogate such plasmas and so opens the door to new diagnostic methods that can be employed for such challenging environments.

## References

- [1] E. V. Barnat and K. Frederickson, “Two-dimensional mapping of electron densities and temperatures using laser-collisional induced fluorescence”, *Plasma Sources Sci. Technol.* **19**, 055015 (2010).
- [2] E. V. Barnat and B. R. Weatherford, “Two dimensional laser-collision induced fluorescence in low-pressure-argon discharges”, *Plasma Sources Sci. Technol.* **24**, 055024 (2015).

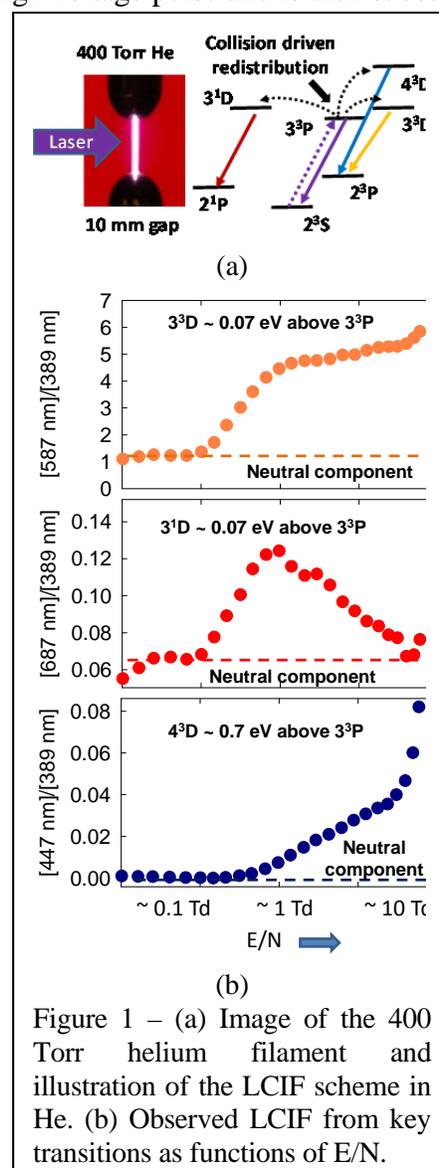


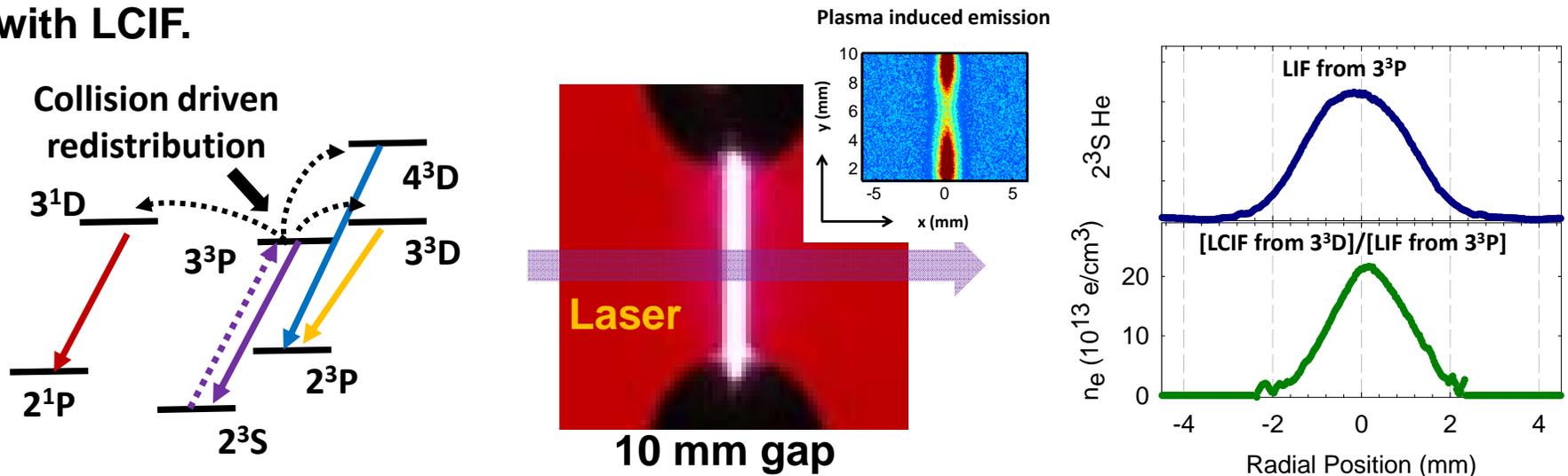
Figure 1 – (a) Image of the 400 Torr helium filament and illustration of the LCIF scheme in He. (b) Observed LCIF from key transitions as functions of E/N.

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**Highlight**

# ULTRASHORT LASER-COLLISION INDUCED FLUORESCENCE IN HIGHLY COLLISIONAL PLASMAS

- Ultrashort (<100 fs) laser excitation of near-atmospheric pressure plasma systems is being investigated and demonstrated.
- Proof-of-principle opens door to diagnostic methods that enable temporal resolution of plasma events on sub-picosecond time scales.
- Electron dependence of laser-collision induced fluorescence (LCIF) has been demonstrated in a highly collisional helium plasma (400 Torr,  $[e] > 2 \times 10^{13} \text{cm}^{-3}$ ).
- Radial profiles of the He( $2^3S$ ) metastables and electron densities ( $n_e$ ) measured with LCIF.



• LCIF scheme

• 400 Torr He filament

• Profiles measured with LCIF

## Plasma Diagnostics and Modeling of Lithium-Containing Plasmas for Deposition of Solid Electrolytes

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Lithium containing solid electrolytes find applications in both energy storage and energy conservation. For example, these electrolytes have potential uses in lithium-ion batteries and in electrochromic windows. Of particular interest are  $\text{Li}_x\text{Si}_y\text{S}_z$  films, which have very high ionic conductivity. Fabrication of these films present many processing and plasma physics challenges. We are depositing these types of films using an argon plasma that also contains lithium bis(trimethyl)silane, silane, and either sulfur vapor or di-tert-butyl disulfide as the sulfur source.

The electron impact induced chemistry occurring in these plasmas is very complex. Using optical emission spectroscopy, modeling and ex situ film characterization we are attempting to distill the most important factors that govern the film composition during plasma deposition. To do this we have set up a tubular capacitively coupled plasma deposition system where the precursor gases in argon are fed from the top, flow through the capacitively coupled plasma and exhaust from the bottom, as shown in Fig. 1. Film is deposited on a substrate placed along the tube walls. The plasma composition changes as the gases flow through the tube and films deposited on the substrate have an axial composition gradient as shown in Fig. 2.

Using a combination of modeling, optical emission spectroscopy and ex situ film characterization we are studying the factors in the plasma that affect the film composition. Specifically, we solve Boltzmann's equation to determine the electron energy distribution function and use these distributions to calculate electron impact rate coefficients. We then use these rates to model the simplified chemistry in the plasma as a function of position. Preliminary results suggest that the Li concentration in the films is higher near the top where the gases enter the reactor (Fig. 2) because Li is generated and transported at higher rates towards the walls (and hence the substrate) than Si. To our knowledge this is the first plasma deposition of a  $\text{Li}_x\text{Si}_y\text{S}_z$  solid electrolyte.

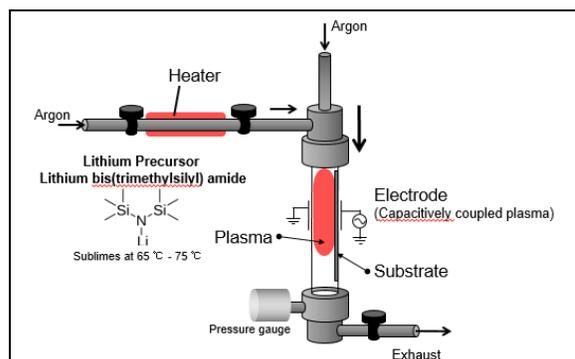


Figure 1 – Schematic of the plasma reactor to study plasma deposition of  $\text{Li}_x\text{Si}_y\text{S}_z$  films.

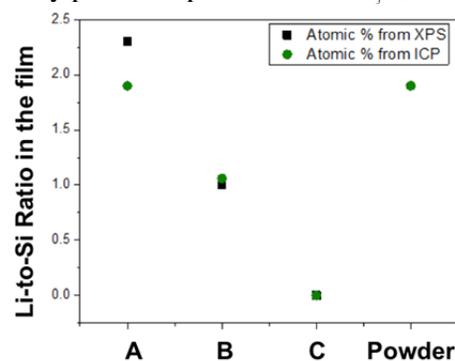


Figure 2 – Li-to-Si ratio in films deposited near the top (A), electrode (B) and bottom (C) of the tube. Composition of powder collected at the reactor exhaust is also shown.

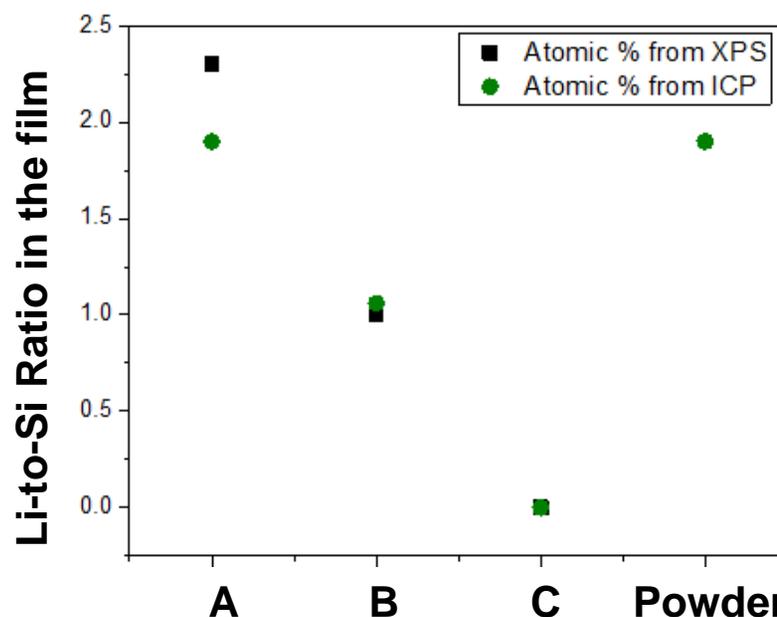
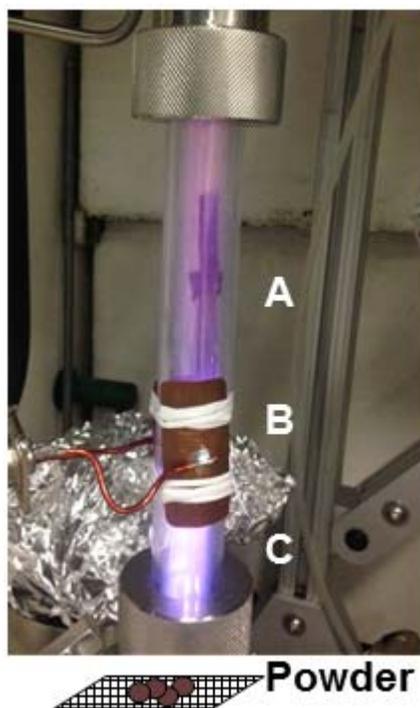
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**Highlight**

# LITHIUM-CONTAINING PLASMAS FOR DEPOSITION OF SOLID ELECTROLYTES FOR BATTERIES

- Using a combination of plasma diagnostics and modeling we are studying Li-containing plasmas and deposition of Li-containing solid electrolytes (e.g.,  $\text{Li}_x\text{Si}_y\text{S}_z$ ) that may be used in Li ion batteries and electrochromic windows.
- We have shown that thin films of  $\text{Li}_x\text{Si}_y\text{S}_z$  can be deposited from a mixture of Lithium bis(trimethylsilyl) amide,  $\text{SiH}_4$  and a S source and Li-to-Si ratio in the film depends on the location of the substrate in the plasma.

- Plasma deposition system.



- Li-to-Si ratio in films deposited at locations A, B and C (left, and in powder collected in the exhaust)