PRECISION
Strategic Research Cluster

Application of Two-photon Absorption Laser Induced Fluorescence to validate actinometry measurements of absolute atomic oxygen number density based on improved EEDFs obtained from PIC simulations.

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Introduction:

- ***Actinometry*** is a non-invasive optical technique that allows absolute atomic oxygen number density [O] determination within a plasma provided certain conditions are met.
- **Problem:** Technique is sensitive to the accuracy of the Electron Energy Distribution Function (EEDF).
- **Maxwellian distribution** is often used for actinometry calculations but this is typically just an approximation.
- **Particle in Cell (PIC)** code is used to generate a more accurate EEDF to improve the actinometry results.
- ***TALIF*** is used as a benchmark to validate the results obtained from actinometry

Actinometry:

- Comparison of the intensity of O emission lines at 884 nm or 777 nm with that at 750 nm obtained from a known concentration of Argon [Ar] within the plasma allows absolute [O] density to be determined.

The expression used for actinometry (including non-radiative de-excitation (k_q) and dissociative excitation (k_{de}) mechanisms) is:

$$[\mathrm{O}] = \frac{\mathrm{I_O}}{\mathrm{I_{Ar}}}[\mathrm{Ar}]\frac{k_e^{Ar}}{k_e^{O}}\frac{1}{\gamma} - \frac{k_{de}^{O}}{k_e^{O}}[\mathrm{O_2}]$$

where

$$\gamma = \frac{c_{(\mathrm{O})}\upsilon_{(\mathrm{O})}A_{ij}^{(\mathrm{O})}\left(k_q^{\mathrm{Ar}}[O_2] + \sum_j A_{ij}^{\mathrm{Ar}}\right)}{c_{(\mathrm{Ar})}\upsilon_{(\mathrm{Ar})}A_{ij}^{(\mathrm{Ar})}\left(k_q^{\mathrm{O}}[O_2] + \sum_j A_{ij}^{\mathrm{O}}\right)}$$

where k_e: Rate coefficient for excitation of upper level via electron collision.
I_o, I_{Ar}: Spectral intensities of O and Ar emission lines from the plasma.
γ: Constant that incorporates optical and geometric parameters such as solid angle, frequency of emitted light, transmission of optics etc.
provided $[o_2]$ *remains constant*.

The determination of [O] depends very strongly on the rate coefficients k_i - all other quantities in the expression essentially remain fixed for a given set of experimental conditions.

Rate constants and EEDF:

- Rate constant k_e is calculated using:

$$k_e = \int_0^\infty f(E)\sigma\sqrt{\frac{2E}{m_e}}\,dE$$

where $f(E)$: Normalized EEDF.
m_e: Electron mass.
σ: Electron collision cross section.
E: Electron energy.

The rate coefficients are sensitive to the form of the EEDF $f(E)$.

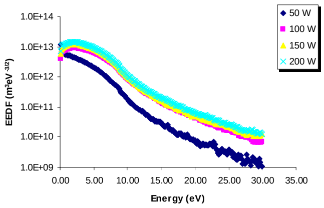
Improved accuracy of EEDF → improved accuracy of actinometry [O] results.

Particle In Cell (PIC) simulation:

- Fluid model approach that uses basic physics of particle interactions to arrive at the plasma conditions.
- Input variables to "tune" the simulation to the plasma are:
  (1) Feedstock gas mixture.
  (2) RF voltage in the chamber.
  (3) Plasma chamber dimensions.
- The Code generates the EEDF, and electron density *ne* for a given set of conditions.
- The calculated *ne* from the code can be compared with a measured value of *ne* obtained using a hairpin probe on the system to validate the simulation.
- Comparable values of the theoretical and experimental *ne* indicate a "good" EEDF for the plasma.

RF Power (W)	n_e (m^{-3})	n_e (m^{-3})
	PIC	Expt
50	2.95E+15	1.35E+15
100	5.56E+15	4.52E+15
150	8.35E+15	7.24E+15
200	1.07E+16	9.19E+15
250	1.25E+16	1.06E+16
300	1.41E+16	1.20E+16

Comparison of n_e measured with hairpin probe with that from the PIC code. The preliminary results are in reasonable agreement and the corresponding EEDFs are plotted in the adjacent figure.



References:

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[2] N S Braithwaite, Pure and Appl. Chem. 62 (1990) 1721.

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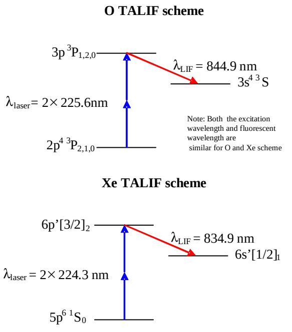
Two-photon Absorption Laser Induced Fluorescence (TALIF):

- **TALIF** allows absolute atomic oxygen number densities to be easily determined if calibrated with an appropriate Noble gas two-photon scheme such as that of Xenon given below.
- Excitation and fluorescent detection conditions must be similar for both O and Xe TALIF.
- The laser must operate at powers that ensure an unsaturated quadratic response from the detection system for both O and Xe.



- [O] is calculated using:

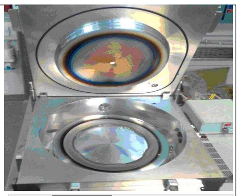
$$n_O = \chi\frac{\mathrm{S_O}}{\mathrm{S_{Xe}}}n_{Xe}$$

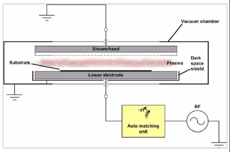
where: S_o, S_{Xe}: measured TALIF signals integrated w.r.t. time, fluorescent wavelength, excitation wavelength and normalised to the square of the laser Pulse energy.

χ is a constant that takes account of the optical transmission of the system T_i and quantum efficiency of the detector η_i at the fluorescent wavelengths λ_i, the two-photon absorption cross sections σ_i and the effective branching ratios a_i.

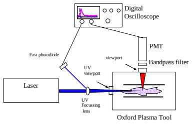
$$\chi = \frac{\mathrm{T_{Xe}}}{\mathrm{T_O}}\frac{\eta_{Xe}}{\eta_O}\frac{\sigma_{Xe}^{(2)}}{\sigma_O^{(2)}}\frac{a_{21}^{Xe}}{a_{21}^{O}}\left(\frac{\lambda_{Xe}}{\lambda_O}\right)^2$$

Experiment:





- Oxford instruments Plasmalab System 100 reactive ion etcher.
- Parallel plate capacitive asymmetric RF plasma system used to process 200 mm wafers.
- Wafer is placed on the lower powered electrode and gas feed through a showerhead designed into the upper ground electrode.
- A feedstock gas mixture comprising 96:4 % O_2:Ar at 100 mTorr was introduced into the chamber and RF power varied.
- TALIF and optical emission spectra were recorded at each setting.

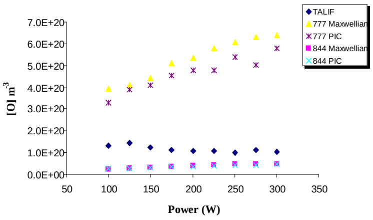


TALIF experiment:

Laser light at 226nm is focussed into chamber using UV optics. The resulting fluorescence at 844 nm is detected using a PM tube. An optical bandpass filter is used to attenuate the background light from the plasma so only the laser induced fluorescence reaches the detector.

Comparison of actinometry results obtained using PIC EEDF and Maxwellian EEDF with TALIF results for [O]:

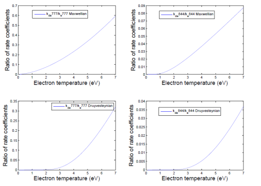
- Absolute [O] number density was calculated using Maxwellian EEDF and PIC EEDF with actinometry.
- Results plotted along with TALIF data for comparison below.



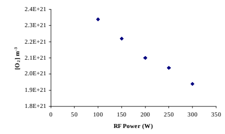
- TALIF measurements show [O] ~ 1 x 10^{20} m^{-3} and decreases slightly with increasing RF power.
- Actinometry results using 777 nm line give largest discrepancy with TALIF [O] results.
- Actinometry results using 844 nm line are significantly closer to TALIF [O] data.
- Actinometry indicates a slight increase in [O] with increasing RF power but TALIF shows [O] decreases.

Discussion:

- The stronger agreement between TALIF and actinometry results at 844 nm is expected as error associated with dissociative excitation is smaller for 884 nm line than 777 nm line as explained by ratio of k_{de}/k_e in graphs.
- The results presented are preliminary and improved EEDFs generated using PIC code should improve agreement between the techniques for absolute [O] density measurement.
- Trend difference can be explained by a drop in O_2 number density in chamber with increasing RF power due to a temperature increase in the chamber. For the purpose of actinometry calculations [O_2] was assumed to remain constant as pressure is constant. However, mass spec data recorded indicate a drop in [O_2] as RF power increases.



Plots of the ratio of k_{de}/k_e for the 777 nm and 844 nm lines. The plots show the values obtained for a Maxwellian distribution and a Druyvestian distribution



Plots of variation in [O_2] with RF power recorded with a mass spectrometer. The data shows a decrease in number density with increasing power which is attributed to gas heating.

Acknowledgement : *"This material is based upon works supported by the Science Foundation Ireland under Grant No.08/SRC/I1411."*