# Characterization of the spatial distribution of excited species at the prepeak and afterpeak time domains in pulsed RF-GD-OES

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## INTRODUCTION

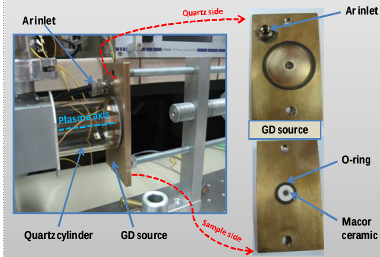
Radiofrequency Glow Discharge (rf-GD) spectrometric techniques are powerful analytical techniques for direct solid analysis of bulk and coated materials, for conducting and isolating samples. The development of pulsed-GD sources has opened new possibilities in GD techniques due to the interesting properties that they present such as less thermal effects, and different time-domains along the GD pulse which are related to different excitation/ionization mechanisms of the species present in the plasma [1].

In commercial rf-GD-OES instruments, the average emission intensity of the whole plasma is acquired and fundamental studies with this disposal give useful but limited information about the plasma. In this work, an in-house experimental set-up provided with a hollow anode source has been developed in order to allow spatially resolved measurements of the emission. Side-on as well as end-on observation of the plasma plume can be performed. The detection system consists of a spectrograph with an intensified charge coupled device (iCCD) synchronized with the rf-generator, allowing time resolved data acquisition. A system of lenses focuses the emission coming from different positions along the plasma plume axis, at distances where the sampler can be found when coupling the GD to a mass spectrometer.

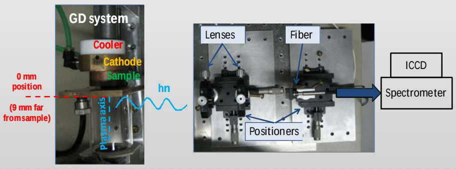
Temporal and spatial distributions of different species have been investigated in pulsed-rf-GD. Emission intensities are measured at different positions of the plasma plume, and also at different times along the rf-GD pulse. In particular, argon and analyte (copper) emission has been evaluated during prepeak and afterglow temporal domains, at different RF pulse frequencies. These results will help to understand in more detail the GD plasma dynamic and, thus to improve the performance of the GD-MS instruments in which the mass transport plays an essential role.

## EXPERIMENTAL SET-UP

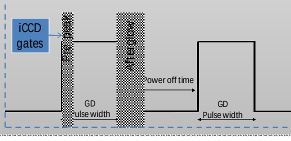
### GD source




### Detection system



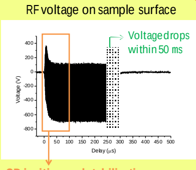

### PULSED GD PARAMETERS



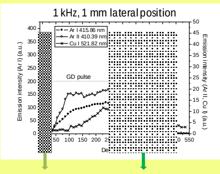

| GD EXPERIMENTAL CONDITIONS | |
|---|---|
| RF forward power | 83 W |
| Ar flow rate | 250 sccm |
| Pressure | 420 Pa |
| Duty cycle | 25 % |
| GD pulse frequency | 125 Hz, 1 kHz, 2.5 kHz & 10 kHz |
| GD pulse width | 2 ms, 250 ms, 100 ms & 25 ms |
| iCCD gate width | 1-30 ms |

## OES pulse profiles & Electrical conditions

RF voltage on sample surface



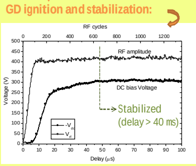

Emission along the GD pulse



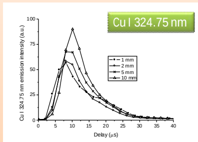

PREPEAK
- 0-30 ms
- Only Ar I and Cu I

AFTERPEAK
- Duration up to 250 ms
- Cu I has two maxima

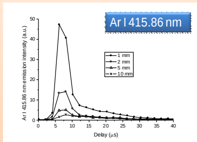
GD ignition and stabilization:



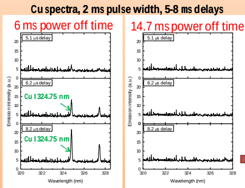

## SIDE-ON PREPEAK EMISSION




Prepeak emission along the plasma axis




Cu spectra, 2 ms pulse width, 5-8 ms delays



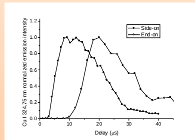

- Cu I and Ar I detection starts simultaneously at 4 ms.
- No dependence on the distance

  no transport phenomena involved?
- Similar behavior at all frequencies

- Cu I prepeak emission due to remaining copper atoms from previous pulses!

2.5 kHz, 100 ms GD pulse width,

### Related to End-on Prepeak emission?

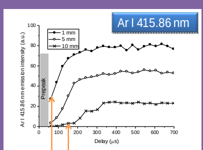



- Side-on early emission is due to the extended and quickly contracted discharge, before dc bias is established!
- End-on is related to the developing dc bias and reduced self absorption [2].

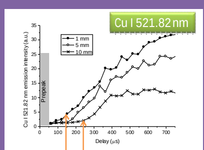
1 kHz, 250 ms GD pulse width,

## PLATEAU ESTABLISHEMENT

✓ After the discharge is confined, the atoms "move" from the anode tube to our observation distances:




- Average speed of about 100 m/s
- Ar excitation origin: about 3 mm in front of sample




- Average speed of about 100 m/s
- Cu atoms origin: about -10 mm, corresponding to cathode surface

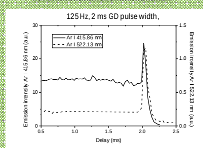
- A delayed emission is registered at further distances
- Transport phenomena are now evident

125 Hz, 2 ms GD pulse width

## SIDE-ON AFTERPEAK EMISSION

### DIFFERENT TRANSITIONS

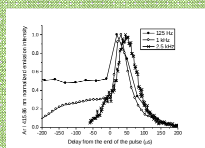
Ar I 415.86 nm: 14.5 eV → 11.5 eV
Ar I 522.13 nm: 15.4 eV → 13.1 eV




- The higher the upper energy level, the higher the afterpeak to plateau intensity ratio

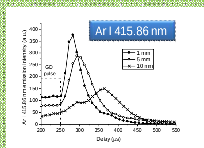
### AT DIFFERENT FREQUENCIES

Ar I 415.86 nm




- Similar afterpeaks at all the frequencies.

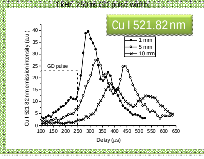
### AT DIFFERENT DISTANCES




Ar I presents one maximum after pulse termination

It "moves" at about 100 m/s

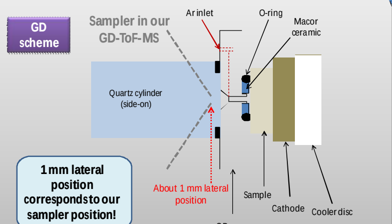
1 kHz, 250 ms GD pulse width,




Cu I presents two maxima after pulse termination

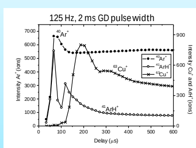
They "move" at about 100 m/s and 50 m/s, respectively.

## POSSIBLE LINK TO MASS SPECTROMETRY?



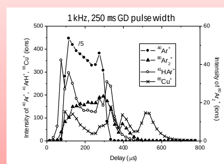

**1 mm lateral position corresponds to our sampler position!**

### Pulsed RF GD-ToFMS profile during PREPEAK




- Possible influence of the extended discharge on the observed MS prepeaks?

### Pulsed RF GD-ToFMS profile during AFTERPEAK




- Ar I and first Cu I OES afterpeak related to $Ar^+$ and $ArH^+$?
- Second Cu I OES afterpeak related to $Ar_2^+$?

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## CONCLUSIONS

- Cu and Ar atomic emission lines show side-on prepeaks due to the extended discharge that takes place for the first 20 ms, before the dc bias is fully established.
- The detection of Cu side-on prepeaks reveals the presence of Cu atoms sputtered during previous GD pulses.
- Transport phenomena are evident when analysing plateau or afterglow emission at different positions along the plasma axis.
- Average speeds for the Cu and Ar "movement" observed during plateau and afterglow are estimated to be about 100 m/s, except for the second Cu afterpeak maximum which seems to move at about 50 m/s.
- The second Cu afterpeak might be related to $Ar_2^+$ peaks observed in GD-ToF-MS. It seems consistent with the relation between Ar and $Ar_2$ diffusion coefficients (factor of about 2), but further research is needed.

**References**

*[1] Ph. Belenguer, M. Ganciu, Ph. Guillot, Th. Nelis, Spectrochim. Acta Part B* ***64****, 623-641 (2009).*

*[2] D. Alberts, P. Horvath, T. Nelis, R. Pereiro, N. Bordel, J. Michler, A. Sanz-Medel, Spectrochim. Acta B, 65 (2010) 533-541.*

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