Imperial College Spectroscopy Group Glow Discharge Studies

Final Report, Imperial College ICSTM

Imperial College was a member of the GLADNET EU Marie Curie Research Training Network – 4 year project, 2008-2011

Work Package 2: project 5
Title: High resolution FT spectroscopy (FTS) studies on Grimm-type GD sources
ESR Early Stage **Researcher**: Sohail Mushtaq
Coordinator: Imperial College of Science Technology and Medicine, London, UK;
Responsible scientist: Dr Juliet Pickering
Other partners: EMPA, LECO, ULMET

Objectives of spectroscopic experimental studies on glow discharge processes
The Imperial College contribution to project 5, work package 2 has focussed on novel experimental studies on glow discharge processes in particular the effects of traces of oxygen on Grimm-type glow discharges.

Summary of the work performed and results of the project
Sohail Mushtaq in Imperial College carried out the first multi-line study of oxygen as an impurity in glow discharge spectroscopy (*GDS*). The results of studies using Fourier Transform Optical Emission Spectroscopy (*FT-OES*) and time of flight mass spectrometry (*ToF-MS*) are reported, investigating the effects of controlled addition (*0-1 % v/v*) of oxygen on observed spectra from a Grimm-type glow discharge, generated in Ar plasma with various pure samples, *i.e.* iron, titanium, copper and gold.
Since, the sample sputter rate (*SR*) affects the intensities of sample lines, controlled experiments were carried out to measure the change in sample *SR* with the oxygen concentration in the glow discharge. Significant changes in the *SR* and the intensities of the carrier gas and sample in the presence of oxygen have been found; these changes are greater than those observed with Ar/H_2 and Ar/N_2 mixtures. It was found that the *SR* for a given Ar/O_2 gas mixture is not proportional to current (see Fig. 1), usually the correct assumption in glow discharge work. This appears to be due to a poisoning effect *e.g.* the formation of an oxide layer on the cathode surface. The changed surface means that this does not imply a breakdown of the Boumans equation; however, users should be aware that under these conditions, the *SR* is not proportional to current.

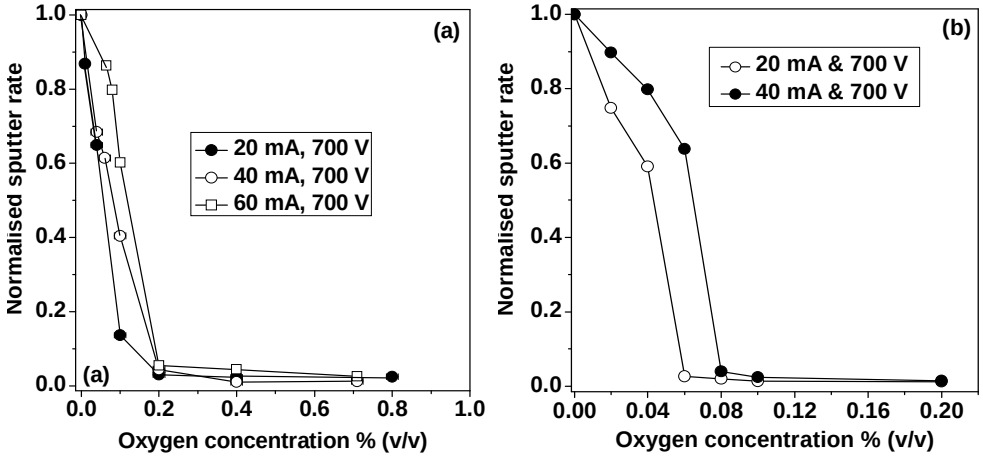

Fig. 1 Normalised sputter rate for (a) iron and (b) titanium as a function of oxygen addition at 700 V and different currents in 4 mm anode tube.

Major changes in the line intensities in emission spectra of iron and argon are observed when O_2 is present even in concentrations as low as ~0.04% v/v in the GD source (Fig. 2). We observed that the populations of the Ar I 4p levels (13.0-13.4 eV) tend to decrease slightly with the addition of oxygen though for many lines the effect is masked by major reductions in self-absorption. The decrease in self-absorption is clearly seen in selected Ar I line profiles with the addition of oxygen (see Fig. 3). On the other hand, the populations in higher energy levels of Ar I (5p) also decrease, but at a more rapid rate. The population of Ar^+ upper energy levels is also reduced with the progressive addition of the oxygen.

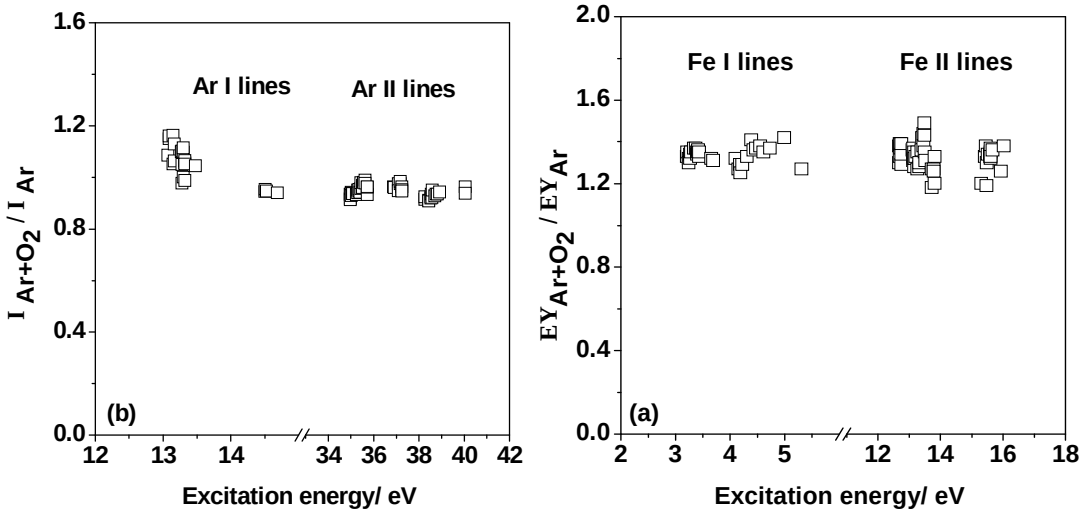

Fig. 2 (a) Intensity ratios (R_I) of Ar I and Ar II vs. total excitation energy (TEE) and (b) Emission yield ratios (R_E) of Fe I and Fe II lines; 700 V and 20 mA and 0.04 % v/v oxygen concentration.

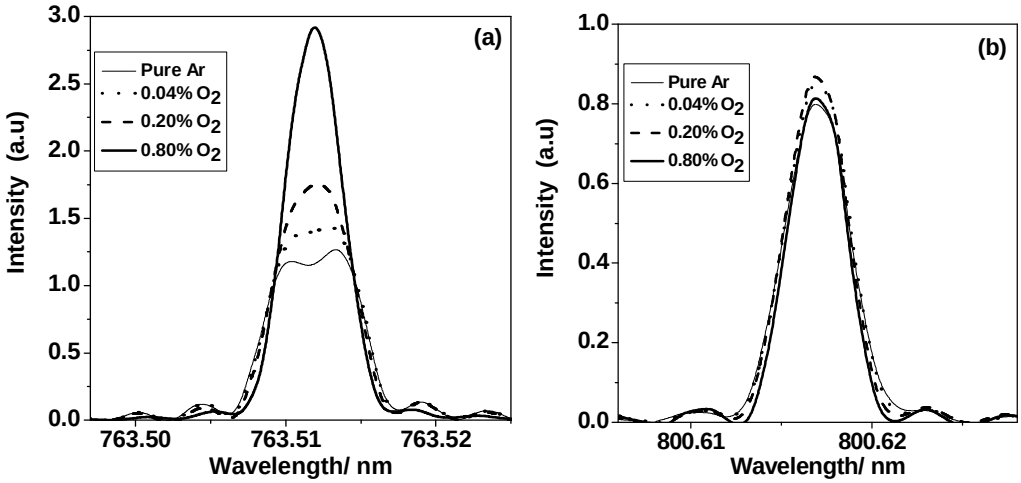

Fig. 3 Example of line profiles of (a) Ar I 763.511 nm, showing self-absorption and (b) Ar I 800.616 nm for various O_2 concentrations. Discharge conditions were 700 V, 20 mA for a 4 mm anode tube diameter.

The intensities of Fe I and Fe II emission lines were reduced due to suppression of *SR*. However, comparing the emission yield ratios, R_E, the excitation of emission lines was slightly increased. The variation in the behaviour of individual levels becomes clearer at higher oxygen concentrations (see Fig.4). We conclude that when oxygen traces are added to a pure Ar plasma significant variations are caused to the excitation processes occurring, and to the relative intensities of spectral lines, particularly those partially or mainly excited by asymmetric charge transfer (*ACT*). It is apparent that the contribution of *ACT* to the selective excitation of certain spectral lines, with TEE (total excitation energy) close to ~13.6 eV, can cause a significant difference in the observed intensities and therefore affect the accuracy of analytical results.

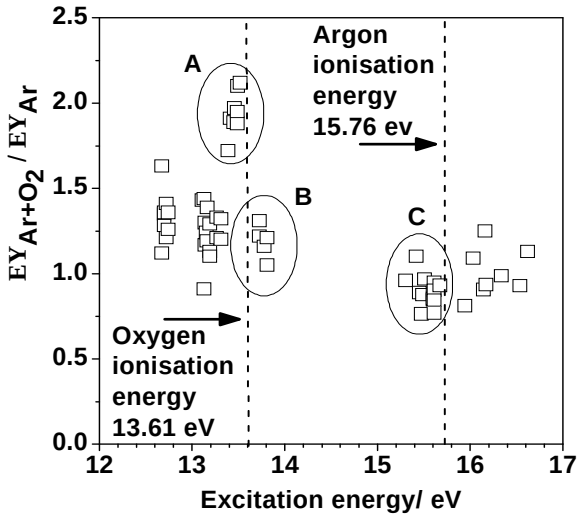

Fig. 4: Plot of EY ratios of all observed Fe II lines plotted against total excitation energy for 0.20 % O_2 for 700 V and 40 mA.

Glow discharge mass spectrometry results

The effects of small amounts of oxygen on argon analytical GD-MS were also studied and compared with the results to optical emission using Fe, Ti, Cu and Au samples. A large and steady decrease of ion signals with oxygen addition was observed (Fig. 5). This decrease was not expected from optical emission data nor was it predicted by models, nor was it observed in a different fast flow source.

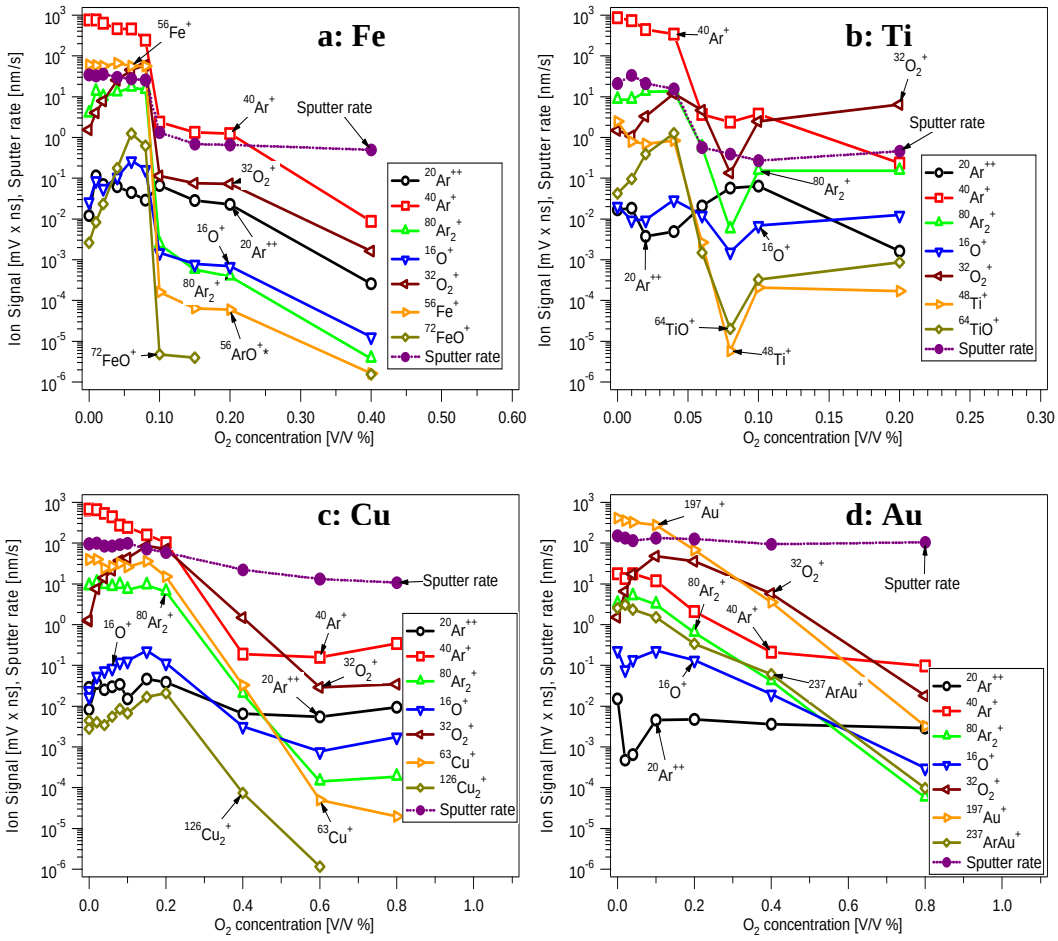

Fig 5. Ion signals and sputter rates vs. oxygen concentration for samples of *a*: Fe, *b*: Ti, *c*: Cu, *d*: Au. The voltage was 700 V and the current 20 mA in all cases.

The results discussed underline the important differences between optical emission detection and mass spectrometry. *GD-MS* instruments are much more sensitive to molecular gases than *GD-OES* instruments due to the quenching of metastable Ar atoms and ion recombination. The comparison to another fast-flow *GD-MS* source shows that differences in the source design can yield very different source characteristics in terms of sensitivity to molecular gases. Better understanding of the fast flow sources is needed to optimise them for more sensitive, more robust analytical performance.

In summary: the first multi line study of the effect of oxygen addition to a glow discharge plasma has been undertaken. Results have been published as follows:

Dissemination of results of the project

Contribution to international conferences

- 52nd Annual Meeting of the APS Division of Plasma Physics, 8th- 12th November, 2010, Chicago, IL, USA.
  Oral talk: "***The role of oxygen in analytical glow discharge: GD-OES and GD-Tof-MS studies***"
  Sohail Mushtaq, Juliet C. Pickering, Edward B. M. Steers, Peter Horvath, James A. Whitby and Johann Michler

- 63rd Gaseous Electronics Conference and 7th International Conference on reactive Plasmas, 4th-8th October, 2010, Paris, France.
  *Oral talk: "**A comprehensive GD-OES and GD-MS study to elucidate the effect of trace molecular gases (O_2, H_2, and N_2) on argon-based glow discharge plasmas***"
  Sohail Mushtaq, Juliet C. Pickering, Edward B. M. Steers, Peter Horvath, James A. Whitby and Johann Michler

- International Glow Discharge Spectroscopy Symposium, August,2010, Albi, France.
  *Oral talk: "**The influence on Grimm-type discharges in argon of oxygen traces, either as an added gas and as a sample constituent***"
  Sohail Mushtaq, Edward B. M. Steers and Juliet C. Pickering

- 20th European Conference on the Atomic and Molecular Physics of Ionized Gases, 13th -17th July 2010, Novi Sad, Serbia.
  *Poster: "**Effects of trace O_2 on emission intensities of sample (iron) and carrier gas (argon) in an analytical glow discharge source***"
  Sohail Mushtaq, Edward B. M. Steers, Juliet C. Pickering and Viktoria Weinstein

- 15th Biennial National Atomic Spectroscopy Symposium- Special one-day meeting, 7th July, 2010, Cambridge, United Kingdom.
  *Poster: "**Influence of oxygen traces, both as an added gas and as a constituent of iron samples on argon Grimm discharges***"
  Sohail Mushtaq, Juliet C. Pickering, Edward B. M. Steers, Peter Horvath, James A. Whitby and Johann Michler

- Colloquium Spectroscopicum Internationale XXXVI, 30th August -3rd September, 2009, Budapest, Hungary.
  *Oral talk: "**Effects of small quantities of oxygen on intensities of Fe I and Ar I lines in analytical glow discharges**"*
  Sohail Mushtaq, Edward B. M. Steers and Juliet C. Pickering

- 14th Biennial National Atomic Spectroscopy Symposium, 7th -9th July, 2008, Brighton, United Kingdom.
  *Oral talk: "**Characterization of ionic and excited neutral species in N_2 plasma generated by 100 Hz pulsed DC source**"*
  Sohail Mushtaq, Sadia Sharif, Riaz Ahmed, M. S. Shah & Nusrullah Khan

Contribution within GLADNET and other places

- Project meeting and training course of the Analytical Glow Discharge Network Meeting, 28th Feb. – 6th March, 2010, Oviedo, Spain.
  *Oral talk: "**Effects of traces of oxygen on Grimm-type glow discharge in argon. Comparison with Ar/H_2 and Ar/N_2**"*
  Sohail Mushtaq, Juliet C. Pickering and Edward B. M. Steers

- Mid-term Review Meeting and Training Course, 26th -30th January, 2009, Thun, Switzerland.
  *Oral talk: "**Study of emission spectra of iron and argon glow discharge containing small quantities of oxygen**"*
  Sohail Mushtaq, Juliet C. Pickering and Edward B. M. Steers

- Mid-term Review Meeting and Training Course, 26th -30th January, 2009, Thun, Switzerland.
  *Poster: "**Study of emission spectra of iron and argon glow discharge containing small quantities of oxygen**"*
  Sohail Mushtaq, Juliet C. Pickering, Edward B. M. Steers, P. Šmíd and V. Weinstein

- Analytical Glow Discharge Network Meeting on Discharge process and Plasma Diagnostic techniques, 21st -23rd August, 2008, Belgrade, Serbia.
  *Oral talk: **"Effects produced by traces of diatomic gases in the plasma gas: Introduction and review of previous work"***
  Sohail Mushtaq, Juliet C. Pickering and Edward B. M. Steers

- Supporting Student Transitions in higher education, Learning & Teaching Conference 2010, 6th July, London metropolitan University, United Kingdom.
  *Combined oral talk: "**Live, study and work in a foreign country"***
  Sohail Mushtaq, Viktoria Weinstein, Tamara Gusarova and Varvara Efimova

- Evan Analytical Group, 12th November, 2010, Syracuse, New York, USA
  *Oral talk: **"GD-MS fast flow sources: need for more sensitive and more robust analytical performance"***
  Sohail Mushtaq

- GSEPS research symposium, 28 July 2009, Imperial College London, UK
  Poster: "**Oxygen as impurity in analytical glow discharge: Can't afford to ignore it"**
  Sohail Mushtaq and Juliet C. Pickering

ESR also attended:

- Piecing it Together Seminar, Thermo Fisher Scientific, 20th November, 2008, London, United Kingdom
- 24th Summer School and International Symposium on the Physics of Ionized Gases, 25th - 29th August, 2008, Novi Sad, Serbia.

Publications

- S. Mushtaq, E.B.M. Steers, J.C. Pickering, P. Šmíd, V. Weinstein and T. Gusarova; *"**Effects of traces of oxygen on Grimm-type glow discharges in argon"*** *J. Anal. At. Spectrom.* 2010, DOI: 10.1039/C0JA00013B.

- V. Weinstein, E. B. M. Steers, P. Smıd, J. C. Pickering and S. Mushtaq; **"*A detailed comparison of spectral line intensities with plane and hollow cathodes in a Grimm type glow discharge source*"**; *J. Anal. At. Spectrom.*; **25**; 2010, 1283–1289; DOI: 10.1039/c003457f

- S. Mushtaq, J. C. Pickering, E.B.M. Steers and V. Weinstein; ***"Effects of trace O_2 on emission intensities of sample (iron) and carrier gas (argon) in an analytical glow discharge source"*** http://www.escampig2010.ipb.ac.rs/papers/P1.15.pdf

In preparation for submission

- S. Mushtaq, J.C. Pickering and E.B.M. Steers, *"**Asymmetric charge transfer involving oxygen ions: selective excitation for ionic spectral lines in an analytical glow discharge source"*** will be submitted to *J. Anal. At. Spectrom.*

- S. Mushtaq, J.C. Pickering and E.B.M. Steers, Peter Horvath, James A. Whitby and Johann Michler *"**The role of oxygen in analytical glow discharges: GD-OES and GD-ToF-MS studies"*** will be submitted to *J. Anal. At. Spectrom*.

- S. Mushtaq, Volker Hoffman, E.B.M. Steers and J.C. Pickering *"**Trace oxygen in analytical glow discharge: Comparison of a sample containing oxide with controlled addition of traces in pure argon"*** will be submitted to *J. Anal. At. Spectrom.*

Summary of visits undertaken by ESR Sohail Mushtaq during the project

- Leibniz Institute for Solid State and Materials Research Dresden, Germany, 14th – 29th June, 2010.

*Purpose**: "Experiments for GD-OES depth profile measurements for calamine samples using GDA650 surface analyzer"*** Supervised by Dr. Volker Hoffmann and Varvara Efimova

- Swiss Federal Laboratories for Material Testing and Research EPMA, Thun, Switzerland, 24th March – 24th April 2010.

*Purpose**: "Experiments and data analysis on glow discharge time of flight mass spectrometry (GD-Tof-MS)"*** Supervised by Dr. Peter Horvath and Dr. James A. Whitby

- Swiss Federal Laboratories for Material Testing and Research EPMA, Thun, Switzerland, 28th October – 08th November 2009.

*Purpose**: "Laboratory experience for the experiments on glow discharge time of flight mass spectrometry (GD-Tof-MS)"*** Supervised by Dr. Peter Horvath and Dr. James A. Whitby

- AQura GmbH, Hanau, Germany 9th November 2009

  *Purpose: "**To attend the steering committee meeting of the GLADNET"***

Workshops attended by ESR Sohail Mushtaq

- *Atomic and Molecular Data Needs for Lighting*, 17th July, 20th ESCAMPIG 2010, Novi Sad, Serbia.
- *Atomic and Molecular Collision Data for Plasma Modelling*, 14th July, ESCAMPIG 2010, Novi Sad, Serbia
- *Using Gas Cylinders Safely within Universities Interactive Workshop*, 4th June, 2008, Imperial College London, UK.
- *Liquid Nitrogen Safely within Universities Interactive Workshop*, 2nd June, 2008, Imperial College London, UK.
- *Atomic Spectroscopy in the Nuclear Industry*, University of Sussex, 7th July, 2008, Brighton, UK.
- *2nd International Workshop on Non-equilibrium Processes in Plasma Physics and Studies of Environment*, Novi Sad, Serbia.
- *Scanning Electron Microscopy and Transmission Electron Microscopy*, EMPA, Thun, Switzerland.
- *Career Development for Research Assistants*, Career Advisory Service, Imperial College London.

Attended by responsible scientist, Dr J C Pickering:

- Project meeting of the Analytical Glow Discharge Network Meeting, 28th Feb. – 6th March, 2010, Oviedo, Spain.
- Mid-term Review Meeting, 26th -30th January, 2009, Thun, Switzerland.
- GLADNET Spring Meeting 2008, 21st-25th April at the IFW Dresden in Germany
- GLADNET autumn meeting September in Belgium, Brussels, 2007 and special GD session of the "ECASIA 07" conference.
- GLADNET kick off meeting, February 2007 in Taormina, Sicily.