Topic number: 1

EFFECTS OF TRACE O_2 ON EMISSION INTENSITIES OF SAMPLE (IRON) AND CARRIER GAS (ARGON) IN AN ANALYTICAL GLOW DISCHARGE SOURCE

S. Mushtaq[1*], J. C. Pickering[1], E. B. M. Steers[2], V. Weinstein[2]

[1] Blackett Laboratory, Imperial College, London SW7 2BW, UK

[2] London Metropolitan University, North Campus, 166-220 Holloway Road, London, UK

*email: s.mushtaq@imperial.ac.uk

The Grimm-type source, in which a plane sample forms the cathode, is widely used in analytical glow discharge (GD) spectrometry to perform surface, interface analysis and compositional depth profiling (CDP) of thin films [1, 2]. A major concern is the possible errors in analytical results due to the presence of trace molecular gases such as O_2, H_2 and N_2. These trace molecular gases can be present in a sample as constituent such as oxide, hydride and nitride. The results of studies using the high resolution vacuum UV Fourier transform spectrometer (FTS) at Imperial College, London, to investigate the effects of added O_2 (0.04-0.2 % v/v) on observed spectra from a Grimm-type GD, generated in an Ar plasma with a Fe cathode (sample) are presented.

To investigate the excitation processes involved for individual energy levels, intensity ratios (line intensities measured in Ar/O_2 relative to those measured in Ar pure) of 67 Fe I, 50 Fe II, 25 Ar I and 50 Ar II emission lines, are plotted against the total excitation energies of the lines in Fig. 1. Since the presence of O_2 greatly reduces the sputter rate, "emission yields" (EY), i.e. intensity divided by sputter rate, of Fe I and Fe II are presented in Fig. 1(a).

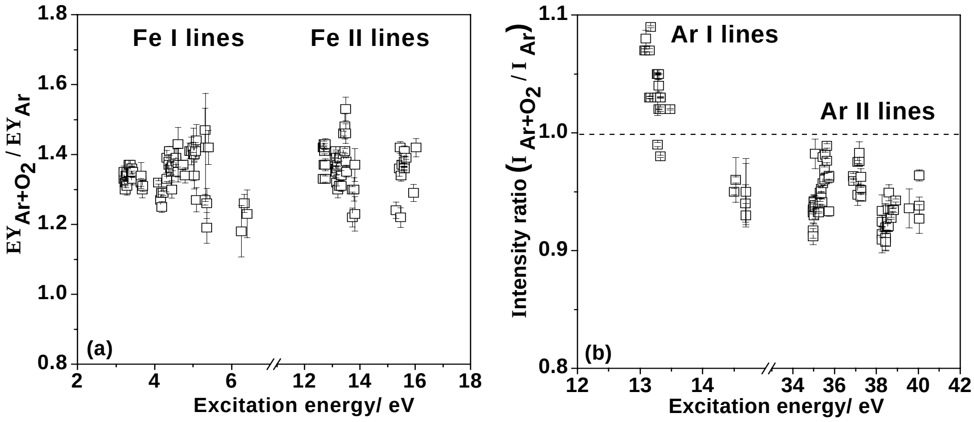

Fig. 1: (a) Emission yields (EY) of Fe I and Fe II lines and (b) intensity ratios of Ar I and Ar II lines, as a function of their excitation energy for GD with 700 V and 20 mA and 0.04 % v/v oxygen concentration.

Preliminary studies of the effect of trace O_2 on intensities of Fe I and Ar I lines in analytical GD are presented in a paper submitted to J.Anal. At. Spectrom. [3], so only a brief summary is given here. The intensities of all Fe I lines decreased due to the reduced sputter rates. However, comparing the EY ratios shows that the excitation of Fe I emission lines was enhanced. A detailed study of spectral line profiles shows a marked reduction in self-absorption of Ar I lines indicating a reduced population of Ar metastables.

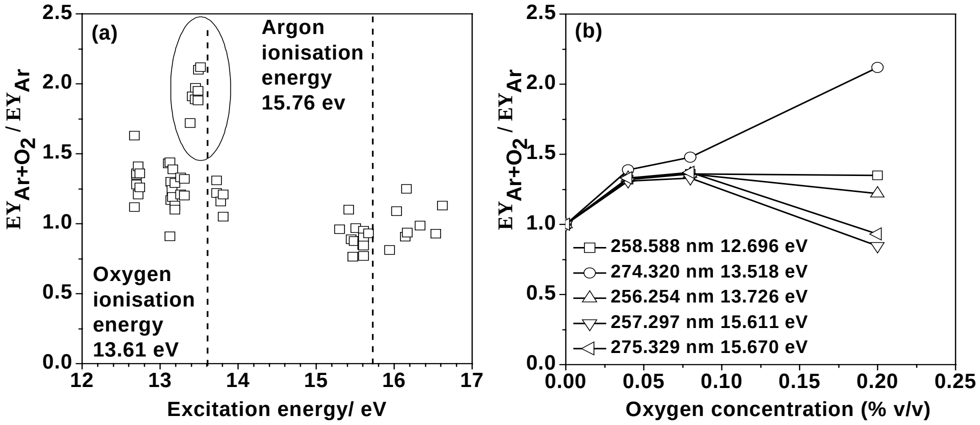

Fig. 2: Results from 700 V and 40 mA discharge: (a) EY ratios of all observed Fe II lines plotted against total excitation energy for 0.20 % O_2 (b) EY ratios of selected lines plotted against O_2 concentration Note: Co-adding of the interferogram reduced the noise level in the intensity measurements and the error in EY ratio due to this is less than the height of symbols. Although, the low sputter rate at 0.20 % v/v gives rise to an error of ~5% in the absolute value of the EY ratio; this will not affect the differences in the behaviour shown by various spectral lines for the same O_2 concentration.

Fe II lines such as 274.320 nm with upper energy close to 13.61 eV (ionisation energy of oxygen) have a significantly greater emission yield in the presence of trace O_2 than in pure Ar. It is suggested that this is due to exoergic asymmetric charge transform with oxygen ions (O-ACT)

i.e. $Fe_o + O^+ \rightarrow Fe^{+*}_{(13.518\,eV)} + O_o + \Delta E$

The probability for ACT is increased when ΔE is small [4] (~ 0.092 eV for 274.320 nm). Steers *et al.* [5] reported a similar result for trace H_2 in argon, showing that ACT involving hydrogen ions (H^+) was a very important selective excitation mechanism for Fe II and Ti II spectral lines with a total excitation energy close to 13.60 eV (ionisation energy of hydrogen).

Lines with total excitation energies close to 15.76 eV (Ar ionization energy), e.g. Fe II 257.297 nm and 275.329 nm, are selectively excited in pure Ar spectra, by ACT with Ar^+

i.e. $Fe_o + Ar^+ \rightarrow Fe^{+*} + Ar_o + \Delta E$

The EY of these lines decreases at higher oxygen concentrations, probably due to a reduced Ar^+ population although this effect is less marked than with H_2.

For Ar II lines (Fig. 1 (b)) a drop in intensity ratio with excitation is observed, indicating that the population of the upper levels is considerably reduced with oxygen concentration even low as 0.04 % v/v. By contrast, in the case of added H_2 [6], Ar II lines become considerably more intense, even though the population of Ar^+ ions is dramatically reduced. We do not yet have information about the population of Ar^+ ions and GD mass spectrometry experiments are planned to investigate the effect of trace O_2 on ion populations in the discharge.

References

[1] T. Nelis and J. Pallosi, 2006, *Applied Spectroscopy Reviews,* **41** 227.
[2] A. Bengtson, 2008, *Spectrochim. Acta, Part B,* **63**, 917.
[3] Mushtaq, Steers, Pickering et al., 2010, submitted to *J. Anal. At. Spectrom.*
[4] J. M. Green and C. E. Webb, 1974, *J. Phys. B*, **7**, 1698.
[5] E. B. M. Steers, P. Šmíd, and Z. Weiss, 2006, *Spectrochim. Acta, Part B*, **61**, 414.
[6] V.-D. Hodoroaba, V. Hoffmann, E. B. M. Steers and K. Wetzig, 2000, *J. Anal. At. Spectrom.*, **16**, 43.

The authors gratefully acknowledge the financial support from the EC funded Research Training Network GLADNET, EC contract MRTN-CT-2006-035459.