The ‘Hydrogen effect’ upon the analysis of copper, iron and titanium as observed by Glow Discharge Time-Of-Flight Mass Spectrometry (GD-TOFMS)

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Introduction

The effects of hydrogen upon analytical glow discharge signals remain interesting both for applications and from a purely scientific perspective. Time-of-flight mass analysis provides a complementary perspective on the chemistry and physics occurring within the plasma, albeit complicated by sampling the plasma through a flow tube and pressure restricting orifice rather than by collecting photons originating from near the cathode.

Method

Hydrogen gas (in argon) at concentrations of up to 0.8 volume per cent was used with a direct current glow discharge in constant current (20 mA), constant voltage (700 V across the discharge) mode using a 4 mm anode with a 2 mm fast flow tube. The discharge was allowed to reach steady-state before data was recorded. The plasma composition was monitored using a time-of-flight mass spectrometer; this prototype instrument is broadly similar to that offered commercially by Horiba with a mass resolving power ~2000 M/ΔM used in these experiments, but can not detect mass/charge ratios below 12 Th (thus ruling out direct monitoring of H^+, H_2^+ and H_3^+). Only charged particles can be detected, and measurements were only carried out for positive ions.

Results

Figure 1: *Results for copper*

Figure 2: *Results for iron*

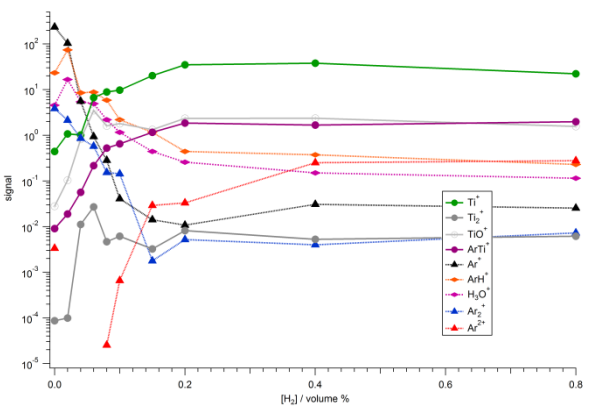

Figure 3: *Results for titanium*

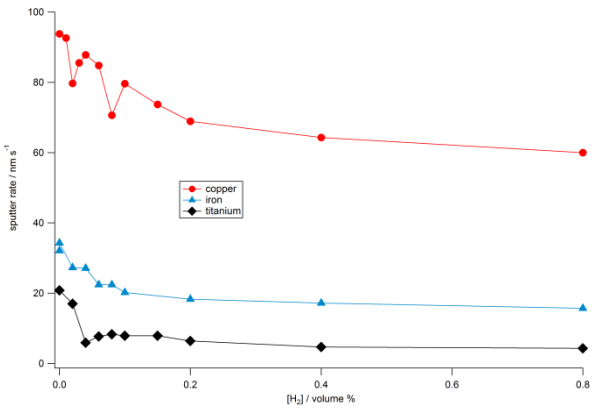

Figure 4*: Sputter rates decrease as a function of hydrogen concentration. The explanation for the deviation from monotonic behaviour for copper and titanium is not clear. Not all conditions gave a stable discharge, but no correlation was observed between discharge instability and ‘unexpected’ sputtering rates.*

- For all three metals the analytical signal increased as low concentrations of hydrogen were added and then became approximately constant. For titanium, this increase in signal was particularly dramatic (x80).
- Sputter rates generally decreased slightly as hydrogen was added, implying that ion yields increased.
- Signals due to ArH^+, H_3O^+ and Ar^+ decreased dramatically over the range of hydrogen concentrations studied. (Although ArH+ and H_3O^+ actually increased at first, peaking at about 0.01 % v/v H_2.)
- ArH^+/Ar^+ ratios go from <0.01 to >10 as hydrogen is added.
- Signals from doubly charged argon ions increased dramatically.
- For all three metals, the signals due to the dimer ion (Cu_2^+, Fe_2^+, Ti_2^+) increased (x100) as hydrogen was added, as, surprisingly, did the signals due to oxides (TiO^+, FeO_2^+).
- No CuH^+, FeH^+, or TiH^+ ions were observed
  - Implies for copper, $[CuH^+] < 0.1\% [Cu^+]$

~~Conclusions~~ Discussion…

- The increase in the analytical signal and reduction in sputter rate is consistent with other reports using a similar technique (Menendez et al., 2005; Saito, 1995, Weinstein poster 2012).
- This increase in analytical signal, and the decrease in sensitivity to changes in the hydrogen concentration, may sometimes be useful
  - No increase in MH^+ interferences observed in these experiments
- The similarity of the data for copper and iron suggests that the chemistry/physics of hydrogen with argon is dominating the behaviour, rather than reactions of the sputtered metal. The different behaviour of the signals from titanium may reflect the greater reactivity with oxygen impurities.
- The simultaneous decrease of Ar^+ and increase of Ar^{2+} suggests that some new charge transfer process becomes dominant, we speculate that H_3^+ may play a role.
  - It is known from optical observations that [Ar*] decreases as $[H_2]$ increases
- The increase in MO+ ions with increasing hydrogen concentration is unexpected: even for a constant amount of oxygen background it seems odd that in a more reducing plasma the concentration of oxide ions should increase.
  - NB presence of Impurities in discharge!
- The decrease in argon ion concentration observed by the mass spectrometer may be due to i) reactions in the afterglow plasma within the flow tube and interface or may ii) reflect a real change in the charge carriers in the glow discharge.
  - If ii), why does sputtering rate remain roughly constant – self-sputtering?
- The behaviour of $[ArH^+]$ is very different than that observed for the GD Element (see poster 5)
- Seems clear that sampling/interface design plays a significant role in determining the abundances of the observed ions

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See also poster P5 “Effect of added molecular gases H2, O2 and N2 (0-1%) on the Thermo Element GD ion signals with an argon discharge” by Weinstein et al.

References

Menendez et al. 'H_2/Ar direct current glow discharge mass spectrometry at constant voltage and pressure' Spectrochimica Acta B, (2005) 60, 824-833.

M Saito 'Effect of Ar/H_2 and Kr/H_2 as discharge gas on the ion intensity in dc glow discharge mass spectrometry' Fresenius J. Anal. Chem. (1997) 357, 18-21.

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