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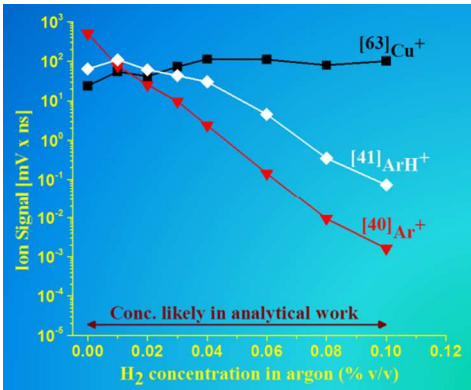
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One sentence highlighting the novelty of the work

‘Hydrogen effects’ are investigated at very low H<sub>2</sub> concentration in an Ar plasma, and the likely discharge mechanisms are discussed.

Colour graphic



## Paper

# A Glow Discharge Time-Of-Flight Mass Spectrometry (GD-TOFMS) study of the 'hydrogen effect' using copper, iron and titanium cathodes

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We report TOFMS investigations on the effects of hydrogen added to a dc GD argon plasma, in detail over the most likely concentration range occurring in analytical work (0 - 0.10% v/v), together with an overview to 0.8% v/v; typical GD-OES discharge condition were used. Many previous studies on the effects of hydrogen in analytical GD-MS used much higher hydrogen concentrations. In this paper, we report for the first time the 'hydrogen effect' on relative ion signal intensities of matrices, plasma and added gas, for very low but analytically important hydrogen concentrations. We investigate the behavior of doubly charged argon ions ( $\text{Ar}^{++}$ ), dimer ions ( $\text{Cu}_2^+$ ,  $\text{Fe}_2^+$ ,  $\text{Ti}_2^+$ ,  $\text{Ar}_2^+$ ) and polyatomic ions ( $\text{ArH}^+$ ,  $\text{CuH}^+$ ,  $\text{FeH}^+$ ,  $\text{TiH}^+$ ), which can play important role in plasma processes. We discuss the probable discharge mechanisms in order to gain a greater understanding of the fundamental processes involved in the ionization of the species observed in this study and their likely effects on analytical results. We propose a mechanism to explain the increase in the matrix signal which occurs if an argon/hydrogen mixture is used as the plasma gas.

## 1. Introduction

The effects of molecular gases ( $\text{H}_2$ ,  $\text{O}_2$  &  $\text{N}_2$ ) on analytical glow discharges (GD) have been examined by many authors in the last few decades with the chief emphasis on the presence of hydrogen in an argon plasma.<sup>1-13</sup> The main results obtained, either by experimental studies or by computer modelling, reveal that the presence of hydrogen in an argon GD affects considerably the electrical characteristics of the discharge, the sputter rate of the analyte, the number densities of the various plasma gas ions and metastable atoms. The effects are greater than those produced by

similar amounts of oxygen or nitrogen. In analytical GD studies, the main focus is on hydrogen investigations because even a small amount of hydrogen (<0.05% v/v) introduced into a plasma by sample contamination or from the sample is sufficient to cause changes in relative intensities of spectral lines of the plasma gas and the analyte constituents and thus causes major analytical errors. The spectral changes in the presence of hydrogen may occur due to changes in selective and non-selective excitation and ionization processes,<sup>14</sup> e.g. Penning ionization/excitation or asymmetric charge transfer (ACT) ionization.

Investigations regarding the general effects of hydrogen in argon plasmas have been reported since the early 1960's.<sup>15-18</sup> Studies of atomic hydrogen line shapes in Ar/ $\text{H}_2$  discharges and the effect of ACT between  $\text{Ar}^+$  and  $\text{H}_2$  were reported by Kuraica and Konjević in the early 1990's.<sup>19,20</sup> However, analytical studies of the 'hydrogen effect' started in the late 1990's, when the first clear effects of hydrogen contamination on line intensities were investigated by Bengtson and Hånström.<sup>21</sup> Later, the effects of hydrogen on the sputter rate, the shape of the crater profiles and the intensities of spectral lines in both argon and neon plasmas were studied comprehensively by Hodoroaba *et al.*,<sup>22-24</sup> with particular emphasis on Cu I and Cu II spectra. Further experimental studies on the effects of hydrogen using GD optical emission spectrometry (GD-OES) and mass spectrometry (GD-MS) have been carried out by Oviedo University,<sup>25-28</sup> London Metropolitan University and Imperial College Spectroscopy research groups.<sup>29-33</sup> A great deal of modelling work regarding the effect of molecular gases on the various plasma species has also been carried out.<sup>34-38</sup> Bogaerts developed a hybrid model for Ar/ $\text{H}_2$  mixtures in a Grimm-type glow discharge, and investigated the effect of  $\text{H}_2$  additions varying between 0.10 and 10%.<sup>38</sup> It appears that, until the work reported here, no dc GD-MS computer simulations or experiments with added hydrogen in the

range 0-0.10% in argon with the discharge parameters commonly used in GD-OES have been published in journals, although such amounts of hydrogen may well occur in analytical practice.

Detailed investigations of excitation and ionization processes in Ar/H<sub>2</sub> plasmas are continuing using MS and OES. Information on ion populations is needed to help in the understanding of the excitation of ionic energy levels and also the excitation of high-lying atomic energy levels by neutralization of ions. Recently Weiss et al.,<sup>39,40</sup> developed a new formalism to describe systematically radiative transitions observed in ionic emission spectra and applied it to draw conclusions about the main excitation processes in GD Mn II and Fe II spectra with pure argon and argon/hydrogen plasmas.

Although much research work has been done on hydrogen in argon plasma and many papers have been published so far using both the OES and MS techniques, there are many unsolved questions regarding GD-MS investigations such as: how are the concentrations of ions of analytical interest behave in dc GD-MS discharges when hydrogen is added in the low concentrations that would be expected in the analysis of typical samples? How do the signals due to other relevant ions, e.g. Ar<sup>+</sup>, ArH<sup>+</sup> behave at very low hydrogen concentrations? What role do the doubly charged argon ions and dimer ions play in argon/hydrogen plasmas? How do complementary GD-MS results with standard GD-OES analytical conditions compare with trends observed with GD-OES studies and what information do they give about processes in the discharge itself? In general, it is important to point out that unlike OES (in which the spectra emitted by the plasma itself is observed) MS can only record the ions present at the sampling orifice. Therefore, the mass spectrum recorded may be very different from the mass spectrum in the discharge, and this effect will depend on the particular GD-MS design.

In this paper, we attempt to answer the above questions using studies on the effects of small amounts of added hydrogen in an argon plasma with a time-of-flight mass spectrometer (TOFMS) for conditions common in GD-OES, *i.e.* a 4 mm diam. crater under constant voltage and current (700 V & 20 mA) conditions. We deliberately included very low hydrogen concentrations (0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.1% v/v) as these are common in analytical work,<sup>13,23,29</sup> particularly if materials have been produced electrolytically. The main purpose of this paper is to understand the 'hydrogen effects' at very low hydrogen concentrations in plasmas. Thus the effects of hydrogen upon analytical GD signals are interesting both for applications and from a purely scientific perspective. Time-of-flight mass analysis provides complementary information 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 the photons originating in the plasma.

From a wider fundamental aspect, and for some analytical applications (e.g. metallic hydrides<sup>23</sup>) it is important to have data with higher H<sub>2</sub> concentrations, so a few (0.15, 0.20, 0.4 and 0.8% v/v) were used in this work. Our recent paper<sup>41</sup> using OES technique has shown that some fundamental processes are only observable at higher molecular gas concentrations.

## 2. Experimental

All the mass spectra generated in Ar and Ar/H<sub>2</sub> plasmas were recorded using the equipment previously described,<sup>42</sup> *i.e.* the GD-TOFMS at the Swiss Federal Laboratory for Materials Science and Technology, (EMPA), Thun. A dc GD was used, with a 4 mm diam. anode and a 2 mm diam. flow tube. The sampling cone is about 20 mm from the crater. 6N argon and a 1% Ar-H<sub>2</sub> mixture (1.00% of 5N5 H<sub>2</sub> and 99.00% of 6N Ar (Carbagas, Gümligen Switzerland) were mixed using three MKS 1479A mass flow controllers: one 500 sccm controller for pure Ar and either a 500 or a 10 sccm controller for the gas mixture (all calibrated for Ar). The purpose-built electronic control system allowed us to change the total flow while keeping the Ar : H<sub>2</sub> mixing ratio constant within the 0.01-1% v/v range. The discharge was allowed to reach steady-state before data were recorded. Although the discharge parameters stabilised in less than 2 minutes, measurements were typically run for at least 5-10 minutes in order to obtain craters deep enough for accurate sputter rate measurements. The average crater depth was determined from an X-Y scan using an Altisurf 500 white light profilometer with 25 x 25 µm resolution. A mass resolving power (M/ΔM) of ~2000 was used in these experiments; ions with mass/charge below 12 Th were outside the range of the TOFMS, thus ruling out monitoring of H<sup>+</sup>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup>. For each hydrogen concentration, we used a new region of the sample to eliminate possibly memory effects due to hydride formation. Initially the particular value of argon/hydrogen ratio was set, then the discharge was ignited and the total flow was adjusted manually in order to adjust the source pressure to give the required current and voltage. The gas pressure was measured downstream of the sample between the flow tube and the sampling orifice using a Pfeiffer TPR260 Pirani gauge and is therefore lower than the gas pressure in the discharge region. Details of the changes in the pressure needed to keep the current and voltage constant with the progressive addition of hydrogen into the argon plasma are given in Table 1.

## 3. Results and discussion

### 3.1 Presentation of the experimental data

The effect of adding small amounts of hydrogen on the ion signals in Ar plasma is shown in Fig. 1 for (a) copper, (b) iron and (c) titanium samples. Data from the most abundant isotopes are plotted for each sample. Because of the large range of ion signal intensities in Ar/H<sub>2</sub> mixtures, a logarithmic intensity scale has been used on the y-axis. The units for ion signals on y-axis are mV x ns. TOFMS had an analogue detection system that records voltage (due to current from the micro channel plates passing through a pre-amplifier) and the nanoseconds arise through the integration of peak widths (which are recorded against time). Values less than 10<sup>-4</sup> mV x ns were not recorded, leading to come breaks in the plots. On the x-axis, an expanded scale is used for the low H<sub>2</sub> concentrations, with a break region, so that the detailed changes in ion signals at low H<sub>2</sub> concentrations are shown clearly. It must be noted that there are different concentration scales before and after the break.

Fig. 1 shows that the major changes in ion signal intensities of matrices, plasma and added gas all occur for small amounts of added hydrogen (<0.1% v/v) in Ar plasma. Thus to understand fully the discharge mechanisms and gas-phase reactions it is desirable that computer simulations should be extended to very small amounts of hydrogen (<0.1% v/v) in argon in future. The change in average crater depths per second of copper, iron and titanium are shown for argon/hydrogen in Fig. 2. In all cases, the sputtering of the analyte materials used decreases with increasing concentration of H<sub>2</sub>.

### 3.2 Specific observations from experimental work

1. The signals due to Ar<sup>+</sup>, ArH<sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> ions decreased dramatically over the range of hydrogen concentrations of most analytical significance. The argon ion signals dropped by 5-6 orders of magnitude with the addition of hydrogen to the discharge. This effect occurs for all three metals used.
2. ArH<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> actually increased at first peaking at about 0.01% v/v H<sub>2</sub>. ArH<sup>+</sup>/Ar<sup>+</sup> ratios go from <0.01 to >10 as hydrogen is added.
3. Despite the decrease in sputter rate of the analyte materials, Fig. 1 shows that for all the three metals the matrix signal increased as low concentrations of hydrogen were added and then became approximately constant up to 0.20 – 0.80% v/v hydrogen concentrations. This is consistent with other reports using a similar technique.<sup>9,43,44</sup> In a similar experiment using TOFMS investigation for much higher hydrogen concentrations (up to 10% v/v) in argon, Menéndez et al.,<sup>27</sup> also reported an increase in analyte ion signals with increasing H<sub>2</sub> concentration.
4. At low hydrogen concentrations in argon, the Ar<sup>++</sup> ion signals are almost negligible however at higher concentrations of hydrogen there is noticeable increase in the ion signals from doubly charged argon ions. The trend observed for the Ar<sup>++</sup> ions is in agreement with the result of Menéndez et al.<sup>27</sup> that the Ar<sup>++</sup> signal increased when 0.5% H<sub>2</sub> was added under constant voltage-pressure conditions. However, no explanation of this increase of Ar<sup>++</sup> ions was suggested and Bogaerts<sup>34,38</sup> does not consider Ar<sup>++</sup> ions in her computer simulations.
5. For all three metals, the signals due to the dimer ions (Cu<sub>2</sub><sup>+</sup>, Fe<sub>2</sub><sup>+</sup>, Ti<sub>2</sub><sup>+</sup>) increased 100 times as hydrogen was added. No CuH<sup>+</sup>, FeH<sup>+</sup>, or TiH<sup>+</sup> ions were observed.

To compare the behavior of ion signal intensities in Ar/H<sub>2</sub> with those in Ar/O<sub>2</sub> discharges, selective ion signals for a copper sample together with the rate of change in average crater depth are plotted in Fig. 3 for various hydrogen and oxygen concentrations, (data for the O<sub>2</sub> case from reference<sup>42</sup>). The electrical conditions were the same for both measurements. In all cases, with added oxygen, the matrix signal decreases, slowly first and then more rapidly at O<sub>2</sub> concentrations greater than 0.2% v/v. By contrast, with added hydrogen, the matrix signal rises, despite a small fall in sputter rate and then remains approximately constant. For all other ion signals, for the same concentration of added molecular gas, the decrease is much greater with Ar/H<sub>2</sub> than with Ar/O<sub>2</sub>; the signals with Ar/O<sub>2</sub> remain effectively constant at concentrations less than 0.2% v/v, i.e.

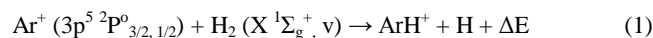
in the range likely to occur in analytical practice. Using Ar/H<sub>2</sub>, the ArH<sup>+</sup> signal at first increases with the addition of H<sub>2</sub>, exceeding the Ar<sup>+</sup> signal, before falling but remaining greater than the Ar<sup>+</sup> signal. For both experiments, an ArH<sup>+</sup> signal of about one tenth of the Ar<sup>+</sup> signal was observed with “pure” argon, presumably due to hydrogen contamination of the source, but with added oxygen it maintained a constant fraction of the Ar<sup>+</sup> signal. No significant ArO<sup>+</sup> signal was observed with added O<sub>2</sub>.

The decrease of matrix ion signals in Ar/O<sub>2</sub> as compared to Ar/H<sub>2</sub> plasma discharges is partially due to increasing surface oxidation and lower sputter rate. Mushtaq *et al.*,<sup>42</sup> suggested that apart from oxidation effects, the reduced ion signals in Ar/O<sub>2</sub> at higher oxygen concentrations are most likely due to gas-phase reactions happening in the afterglow-like plasma in the flow tube and enhanced recombination due to lower electron energies. By contrast, in Ar/H<sub>2</sub> plasmas, the matrix ion signal remains high even at high H<sub>2</sub> concentrations.

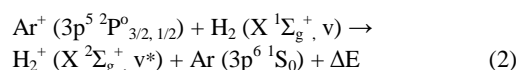
### 3.3 Discussion on discharge processes

A number of possible reasons for the changes in the observed ion signals with the addition of molecular gas to an argon plasma are reported in refs.<sup>40,42</sup> Bogaerts has also performed computer simulations and described in detail the relative contributions of various production and loss processes for the different plasma species in Ar/H<sub>2</sub> discharges in the Grimm-type configuration.<sup>38</sup> In addition to the available information regarding the plasma processes in Ar/H<sub>2</sub> discharges, we will specifically discuss here plasma processes for those species which are mentioned in section 3.2.

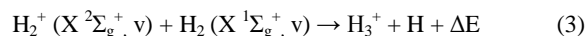
The main loss processes affecting the Ar<sup>+</sup> signal are<sup>45</sup>:



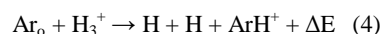
which dominates at low energies, and ACT



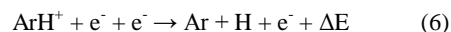
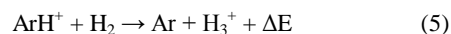
ArH<sup>+</sup> ions are a direct product of process (1), whereas process (2) also leads to the production of ArH<sup>+</sup> through the further steps:



followed by:



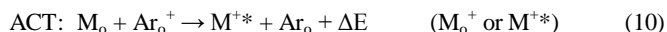
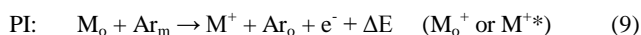
We believe that these multiple paths are responsible for the complex relationship between the Ar<sup>+</sup> and ArH<sup>+</sup> signals. On the other hand, the main loss processes affecting the ArH<sup>+</sup> ion signal are proton transfer, three body neutralization and collision between ArH<sup>+</sup> with Ar<sup>+</sup> ions as:



To look specifically for the possible explanation of the increase of matrix ion signal in Ar/H<sub>2</sub> plasmas (0.01-0.10% v/v), we have to discuss initially the processes which are responsible for the production of matrix ions in pure argon, namely: electron impact



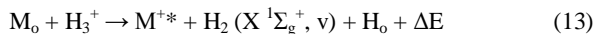
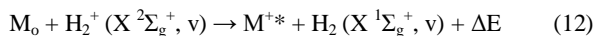
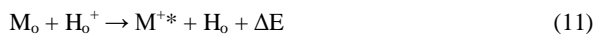
excitation (EI), Penning ionization (PI) and asymmetric charge transfer (ACT):



where  $M_0$ ,  $\text{Ar}_0$  are ground state atoms, e.g., M from the sputtered sample such as Cu, Fe or Ti, \* denotes an excited state,  $m$  a metastable atom,  $M_0^+$  a ground state ion and  $\Delta E$  the kinetic energy released in the collision. In Ar/ $\text{H}_2$  plasmas, there are two factors which actually lead to a decrease of matrix ions. Firstly, the decrease in the sputter rates of analytes used (see Fig. 2), correspondingly decreasing the number density of analyte atoms available for ionization; secondly, the contributions from the processes listed above are reduced in Ar/ $\text{H}_2$  plasmas, as the presence of hydrogen in an Ar plasma results in the reduction of the  $\text{Ar}_m$  and  $\text{Ar}^+$  number densities.<sup>38,46-47</sup> Despite this, an increase in matrix ions is observed and this shows that in Ar/ $\text{H}_2$  discharges, supplementary processes must be occurring for the production of matrix ions.

The increase of pressures in Ar/ $\text{H}_2$  discharges required to keep the voltage constant at constant current, may change the population of plasma species which correspondingly affect the matrix ions. However, for an Ar/ $\text{H}_2$  mixture, using dc GD-TOFMS at constant pressure and voltage, Menéndez *et al.*<sup>27</sup> reported that though there are reduced sputtering rates and currents, still there are higher ionic signal for analyte elements in Ar/ $\text{H}_2$  mixtures than in pure Ar plasmas. This negates the argument that the increase in analyte ion signals in Ar/ $\text{H}_2$  signal could be due to increase of  $\text{Ar}_m$  atoms (correspondingly increasing the contribution of PI in Ar/ $\text{H}_2$ ) as speculated by Saito.<sup>43</sup> Moreover, using OES, Mushtaq *et al.*,<sup>46</sup> have shown the changes in self-absorption of Ar I spectral lines (see Fig. 3 of ref. 46), resulting in quenching of  $\text{Ar}_m$  atoms, due to presence of  $\text{H}_2$  and  $\text{O}_2$  in argon plasmas. The  $\text{H}_2$  concentrations and discharge conditions used in the experiments reported here are similar to those reported in ref. 46.

From the above discussion, it appears that another process must be taking place in the production of matrix ions in the presence of hydrogen in an Ar plasma. Moreover, the fact that the increase in matrix ion signal is observed for  $\text{H}_2$  but not for  $\text{O}_2$  (see Fig. 3), suggests it is not linked with the main plasma gas but with the added gas. We propose that in Ar/ $\text{H}_2$  discharges, in addition of processes mentioned previously in eqn. 8-10, further processes are involved, namely  $\text{H}^+$ -ACT (11) &  $\text{H}_2^+$ -ACT (12), non-resonant ionization by  $\text{H}_3^+$  (13) and neutralization of doubly charged matrix ions ( $M^{++}$ ) (14) and could be contributing for the increase of matrix ion signal, i.e.



where the subscript  $_0$  and superscript  $*$  represent ground and excited state respectively and superscripts  $+$  singly ionized and  $++$  doubly ionized states, and  $\Delta E$  is the energy released (exoergic) or absorbed (endoergic). For ACT,  $\Delta E$  must be small, so only particular ionic energy levels can be excited. Thus  $\text{H}^+$ -ACT can produce excited Fe

and Ti ions.<sup>30</sup>  $\text{H}_2^+$ -ACT can produce excited ions of Fe, Ti and Cu. Thus these processes are element specific. On the other hand, in process (13), there is additional third particle ( $\text{H}_0$ ), which can take away the excess energy, therefore this process is not energy level specific and thus not specific to particular elements.

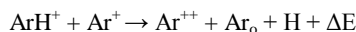
Process (14) is dependent on the population of double ionized matrix ions. We did not record these in our MS experiments. However, Weinstein<sup>44</sup> carried out an extensive investigation on the effects of added hydrogen, oxygen and nitrogen on the ion signals using a ThermoFisher Element GD system, with analogous electrical conditions (700 V, 80 mA for an 8 mm diam. crater). She showed that the population of doubly ionized matrix ions ( $M^{++}$ ) was many orders of magnitude less than of singly ionized matrix ions ( $M^+$ ), so the neutralization of  $M^{++}$  cannot make a significant contribution to the  $M^+$  population. The contributions from the processes mentioned in eqn. 11-13 will depend on the relative populations of  $\text{H}^+$ ,  $\text{H}_2^+$  and  $\text{H}_3^+$  ions and hence on the amount of added hydrogen and the discharge conditions used.

In our MS experiments, the TOFMS could not record ions with mass/charge values below 12 Th, (thus ruling out direct monitoring of  $\text{H}^+$ ,  $\text{H}_2^+$  and  $\text{H}_3^+$ ). However, Weinstein<sup>44</sup> recorded  $\text{H}^+$ ,  $\text{H}_2^+$  and  $\text{H}_3^+$  signals. As the concentration of hydrogen added to the plasma gas increases, the  $\text{H}_2^+$  signal at first increases until the concentration added is  $\sim 0.3\%$  v/v and then either remains constant or falls significantly. Independent of matrix element, for almost all hydrogen concentrations, the  $\text{H}_3^+$  signal at least one or two orders of magnitude greater than the  $\text{H}^+$  and  $\text{H}_2^+$  signals. We therefore propose that  $\text{H}_3^+$  ions are the main cause of the increase population of matrix ions when hydrogen is present in the discharge. This is also in agreement with the difference between the effects of added hydrogen and oxygen. Processes analogous to 11, 12, and 13 could occur for added oxygen, but there are no major discharge processes producing  $\text{O}_3^+$  ions and therefore no increase in matrix ions when oxygen is added to an argon discharge. Moreover process 13 can continue in the flow tube, explaining the maintenance of a high matrix signal at higher hydrogen concentrations.

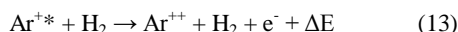
What remains to be discussed are the doubly charged argon ions in Ar/ $\text{H}_2$  discharges; it was observed that at higher hydrogen concentration in argon, the  $\text{Ar}^{++}$  ion signal increases significantly and at  $0.8\%$  v/v hydrogen concentration in argon exceed that of  $\text{Ar}^+$ . This trend has been observed when three different matrices (Cu, Fe & Ti) as cathode samples are used and was also observed previously by Weinstein,<sup>44</sup> although the signal intensities and the intensities changes recorded with the TOFMS instrument are much smaller than those recorded with the Element GD. (This could well be due to loss of the  $\text{Ar}^{++}$  ions in the flow tube of the TOFMS). No increase in  $\text{Ar}^{++}$  ion signals is observed in the case when small amounts of oxygen or nitrogen are present in an argon plasma.<sup>42,44</sup> Bogaerts and Gijbels have developed a two dimensional model for calculating the behavior of  $\text{Ar}^{++}$  in a pure argon dc GD at significantly lower pressures and somewhat lower currents than those used in the present study.<sup>48</sup> They considered a range of pressures and currents and reported that the concentration of  $\text{Ar}^{++}$  never exceeded a few % of the  $\text{Ar}^+$  ion concentration. They suggested that  $\text{Ar}^{++}$  ions almost exclusively formed by electron impact ionization from  $\text{Ar}_0$  atoms,

and they become primarily lost by diffusion and subsequent recombination at the cell walls. Bogaerts did not consider  $\text{Ar}^{++}$  ions in her later publications on the effects of added molecular gases.<sup>34,36,38</sup>

It is not yet clear that what could be the reason for an increase of  $\text{Ar}^{++}$  ions in  $\text{Ar}/\text{H}_2$  discharge. It could be due to the process (7) as:



Alternatively, collisions between the long-lived highly excited argon ions (Rydberg states of  $\text{Ar}^+$ ) with the hydrogen molecules could be the cause.<sup>49-50</sup>



The observation of significant  $\text{Ar}^{++}$  populations in  $\text{Ar}/\text{H}_2$  discharge means suggest that this species must be included in future modelling calculations of  $\text{Ar}/\text{H}_2$  discharges. Only brief information about the  $\text{Ar}^{++}$  ion signals is given, however, the comprehensive studies to understand the mechanism and its comparison with results those observed with controlled addition of oxygen in argon will be discussed in a future paper.

#### 4. Summary and conclusions

Experimental data on the changes in populations of a number of ionic species when hydrogen (up to 0.2% v/v) is added to an argon GD plasma, obtained using a GD-TOFMS are reported and the reasons for the changes discusses. The increase in the analytical ion signal and reduction in sputter rate is consistent with other reports of other similar experiments. This increase may be useful in analytical practice if the increase in analyte ions is greater than the matrix ions.<sup>1</sup> The similarity of the data for three different sample matrices suggests that the chemistry/physics of the reactions of hydrogen with argon is dominating the behavior, rather than reactions of the sputtered metal. The suggestion by Saito<sup>43</sup> that the increase in matrix signal is due to an increase of metastable Ar atoms is ruled out by the experimental result that the  $\text{Ar}_m$  population is reduced by the addition of hydrogen. We propose instead that the increase is due to non-resonant ionization by  $\text{H}_3^+$  ions. Further, the simultaneous decrease of  $\text{Ar}^+$  and increase of  $\text{Ar}^{++}$  suggests that some new plasma process becomes significant in the discharge. The differences between the present results and those using the Element GD reported by Weinstein<sup>44</sup> show that the sampling/interface design plays a significant role in determining the observed ion signals, although this does not affect analytical results as the instruments are calibrated appropriately.

#### Notes and references

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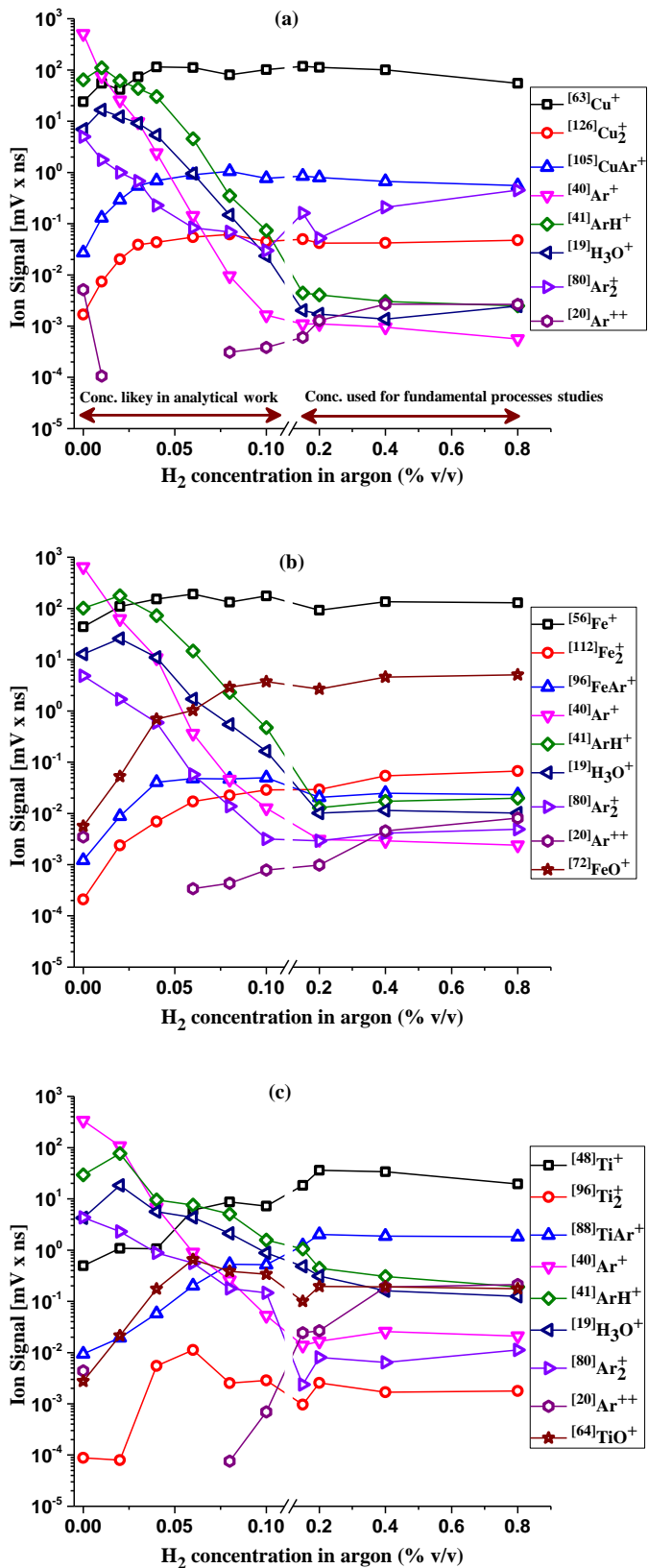


Fig. 1 Plots of ion signals vs. hydrogen concentration for samples of (a) copper, (b) iron, and (c) titanium. The voltage was 700 V and the current was 20 mA in all cases.

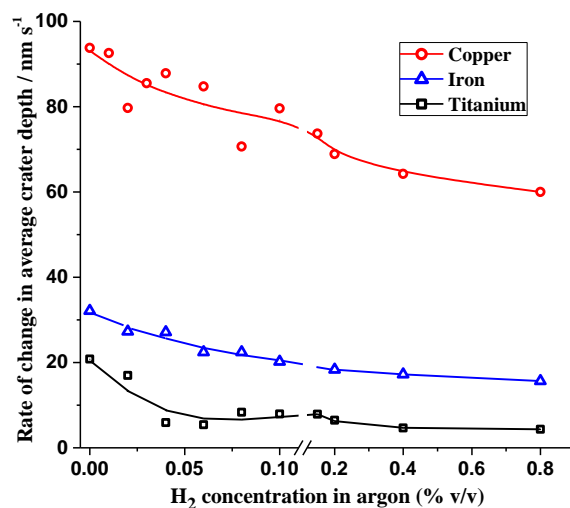


Fig. 2 Change in average crater depth per second of metals as a function of hydrogen concentration. The voltage was 700 V and the current was 20 mA in all cases. Not all conditions gave a stable discharge, but no correlation was observed between discharge instability and 'unexpected' sputter rates.

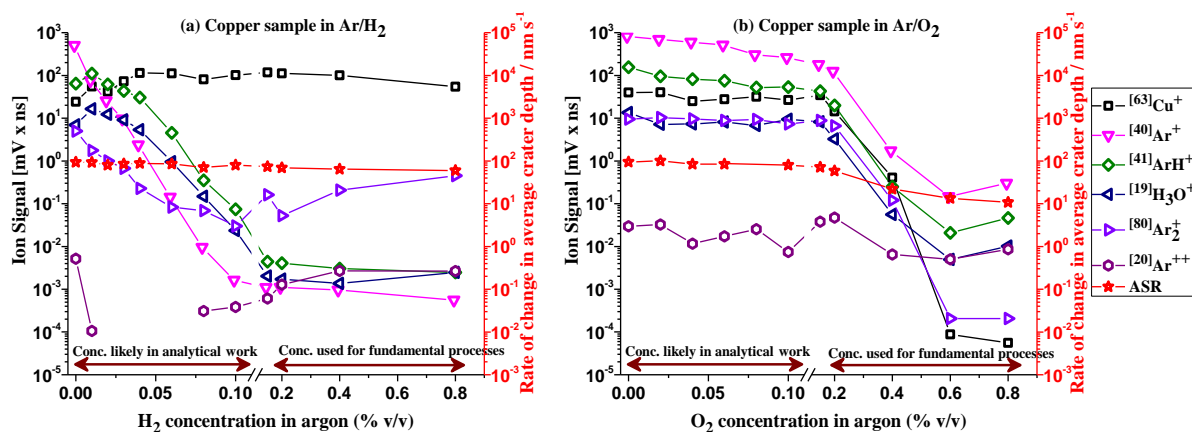


Fig. 3 Selected ion signals and rate of change in average crater depth (ASR) vs. (a) hydrogen & (b) oxygen concentration for copper sample. The voltage was 700 V and the current was 20 mA in all cases.

**Table 1 Variations of the measured gas pressure during the experiments in Ar/H<sub>2</sub> with copper sample at constant dc electrical parameters (20 mA and 700 V) in GD.**

H <sub>2</sub> conc. in Ar (% v/v)	Ar flow rate /sccm	Ar/H <sub>2</sub> flow rate /sccm	Measured gas pressure /mbar (±0.05)
0	144.6	0	1.34
0.01	138.2	1.38	1.30
0.02	125.3	2.55	1.23
0.03	146.0	4.50	1.36
0.04	146.2	6.06	1.37
0.06	149.4	9.48	1.41
0.08	140.6	12.2	1.39
0.10	142.0	15.7	1.41
0.15	165.1	28.8	1.59
0.20	170.5	42.4	1.69
0.40	99.0	65.5	1.44
0.80	33.0	130.5	1.44