

The effect of hydrogen and nitrogen on emission spectra of iron and titanium atomic lines in analytical glow discharges†

Petr Šmíd,^{*a} Edward Steers,^a Zdeněk Weiss,^b Juliet Pickering^c and Volker Hoffmann^d

Received 5th March 2008, Accepted 4th June 2008

First published as an Advance Article on the web 21st July 2008

DOI: 10.1039/b803812k

It is now well known that traces of molecular gases such as hydrogen or nitrogen can affect significantly the electrical characteristics, sputtering rates and relative intensities of emission lines in glow discharge optical emission spectrometry (GD-OES). These changes, caused by the molecular gases which are very often present in the discharge for various reasons, have a serious impact on the accuracy of analytical results. Therefore, it is important to describe these effects in detail and to try to understand the processes involved. The results presented in this paper focus on the effects of hydrogen and nitrogen on intensities of *atomic* emission lines of iron and titanium. In the case of hydrogen, when intensity ratios (intensities measured in argon–hydrogen relative to those measured in pure argon) are plotted against the excitation energies of the lines, these intensity ratios increase with the excitation energy between approx. 3 and 5 eV for both elements studied. Furthermore, in the case of iron, several emission lines with the excitation energy between 5.3 and 5.6 eV are strongly enhanced in the presence of hydrogen. It has been also observed that this effect is more pronounced at lower currents. On the other hand, it has been found that nitrogen does not have any similar effect: the gradient of the intensity ratios of both elements is negligible or even negative and no emission lines are enhanced in the presence of nitrogen. A comparison was also made between direct current and radiofrequency powered glow discharges and very similar trends have been obtained.

Introduction

Analytical glow discharges in Grimm-type configuration have been successfully used for direct solid sample analysis and for depth profile analysis of coated materials for several decades. Although this technique, which uses either an optical emission spectrometer (GD-OES) or a mass spectrometer (GD-MS) for the determination of chemical composition, is now well established, the number of papers published in recent years is evidence that this method is still progressively developing.¹ One of the areas of great importance is the effect of molecular gases (hydrogen, nitrogen and oxygen) on the characteristics and performance of the analytical glow discharge. These gases can be present in the discharge due to contamination of the source by residual moisture, atmospheric gases or by the vapours from the pump oils; moisture or organic impurities can be adsorbed on the surface of the sample, but, most importantly, these molecular gases can be present in the sample as its constituents. The contamination of the source is particularly an important issue when very thin surface layers (~nm) are analyzed because the first few milliseconds of the analysis are usually affected by

the source/sample surface contamination. To some extent this can be overcome by modification of the source² but detailed knowledge about the effects and the processes involved when a small amount of a molecular gas is present in the discharge is necessary. Indeed, it has been shown^{3–10} that molecular gases can affect the discharge conditions significantly which complicates interpretation of the results and can reduce the accuracy of the method.

The effect of molecular gases on the analytical glow discharge has been studied intensively in the last few years with the focus on the effect of hydrogen. The main results on the effect of hydrogen obtained both experimentally and from numerical models have been recently summarised in a review article with numerous references.³ A number of papers have been also published on the effect of nitrogen and oxygen, some of the results have been summarised in a review article.⁴ More recent findings on how nitrogen and oxygen affect the intensities of analyte and argon emission lines, sputtering rates and shapes of sputtered craters can be found in ref. 5–9. Indeed, of the three molecular gases mentioned above, hydrogen has the greatest impact on the discharge characteristics. It affects electrical characteristics of the discharge, sputtering rate of samples and the intensities of emission lines of sample and working gas atoms and ions. Not only does hydrogen affect relative intensities of spectral lines of different elements differently, but also relative intensities of individual emission lines of the same element can behave in various ways. This has been already reported by Bengtson and Hånström in 1998.¹⁰ Some of the changes caused by the presence of hydrogen in the discharge have been predicted by numerical models:¹¹ number densities of electrons, argon ions and argon

^aLondon Metropolitan University, 166-220 Holloway Road, London, UK N7 8DB

^bLECO Instrumente Plzeň spol. s r.o., Plaská 66, 323 25 Plzeň, Czech Republic

^cImperial College London, Prince Consort Road, London, UK SW7 2AZ

^dLeibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

† Presented at the 2008 Winter Conference on Plasma Spectrochemistry, Temecula, CA, USA, January 7–12, 2008.

metastable states are reduced in the presence of hydrogen, whereas the population of argon hydride ions (ArH^+) is significantly increased due to the transfer of hydrogen atom between argon ion and hydrogen molecule. Such changes, which can have a serious impact on analytical results, can be corrected in commercial quantification algorithms.¹² These algorithms are based on empirical data obtained under particular experimental conditions and for selected analytical lines. Therefore, they can provide accurate results in some applications but for further improvements of analytical procedures, deeper understanding of the physical processes linked with the effects of hydrogen on glow discharges is essential.

In the current paper, the effects of hydrogen and nitrogen on many lines in the optical emission spectra of iron and titanium are reported, focusing mainly on atomic emission lines. The effect of hydrogen on ionic lines of these two elements was treated in an earlier paper.¹³ The effect of molecular gases was investigated by comparing optical emission spectra from discharges running in pure argon and in mixtures of argon with small controlled amounts of hydrogen or nitrogen with pure iron and titanium samples. For this work, both dc and radiofrequency power supplies were used and the results for the two cases were compared. Finally, a sample containing hydrogen as a constituent (TiH_2) was sputtered in a pure argon discharge and the recorded spectra were compared to those obtained with pure titanium sputtered in the pure argon discharge. The effect of molecular gases on the sputtering rate of iron and titanium was also investigated.

Papers published so far presenting results of the effect of hydrogen on iron and titanium emission spectra have focused on a few selected emission lines of these two elements only.^{14,15} In our study, analysis of a large number of emission lines was undertaken in order to describe the overall picture of the changes, and also, to attempt to give some possible explanations of the effects observed. Furthermore, in recent years, new commercial analytical instruments with CCD detection are becoming available where emission lines within the spectral range covered can be selected for each analyte which is a significant difference compared to the instruments with polychromators with fixed and pre-selected emission lines. Therefore, there is a need for more detailed knowledge about the overall behaviour of the emission lines of a particular element. Also, this information is essential in order to understand processes which take place in the discharge when a molecular gas is present.

Experimental

The effect of hydrogen and nitrogen on the analytical glow discharge was investigated in three separate experiments all of which showed similar trends: at Imperial College London (IC) using a Grimm type glow discharge source with a dc excitation, at Leibniz Institute for Solid State and Materials Research Dresden (IFW) using a Grimm type glow discharge source with either a radiofrequency (rf) or a dc excitation, and at LECO Instrumente Plzeň using a commercial GD-OES instrument. Details of the individual experiments are given in the following paragraphs.

Most of the optical emission spectra were recorded using the vacuum UV Fourier Transform Spectrometer (FTS) at IC for

which a free-standing standard Grimm-type glow discharge source running in direct current (dc) excitation mode was used. The inner anode diameter of this source was either 4 or 8 mm; the data presented here are mostly from the 4 mm anode tube. The plasma gas was supplied to the source *via* a mixing system using three mass flow controllers (MKS Instruments, Inc.) with different flow ranges: 800, 200 and 20 sccm. Various hydrogen or nitrogen concentrations were obtained by mixing pure argon (purity 5.0) with a mixture of argon with 2% v/v hydrogen or nitrogen. The pressure was measured by a capacitance diaphragm gauge, Baratron (MKS Instruments, Inc.), with a pressure range up to 10 Torr, connected directly to the body of the glow discharge source. Stainless steel tubing was used for all gas connections; even so, traces of OH bands were sometimes observed with pure argon. A liquid nitrogen cold trap was installed on the gas inlet line to remove any possible moisture from the gas; this removed all traces of OH bands. A current stabilized dc power supply was used. The discharge was operated in constant current–constant voltage mode so that the overall pressure had to be adjusted to maintain the required discharge voltage when a molecular gas was admixed. The source was viewed end-on and an image of the cathode was focused on the entrance aperture of the FTS instrument with a magnesium fluoride lens.

Exact details of the FTS instrument can be found elsewhere;¹⁶ only brief information is given here. The spectral range available is from about 145 nm up to 900 nm. However, in these experiments we used mainly the range from about 200 nm up to 600 nm. The best available spectral resolution was 0.035 cm^{-1} , independent of wavelength. This corresponds to a chromatic resolving power of 1.4×10^6 and a resolution of 0.14 pm at 200 nm but normally a lower resolving power, sufficient to fully resolve the lines, was used. Two wavelength ranges ($\sim 200\text{--}300$ nm and $\sim 300\text{--}580$ nm) were selected for which appropriate photomultipliers and, where necessary, optical filters were used.

In a complementary study, similarities and differences between dc and rf discharge were investigated. Namely, the effect of molecular gases on the electrical characteristics and optical emission of the rf glow discharge was studied. For this, a Grimm-type glow discharge source with integrated voltage and current probes, developed at IFW Dresden and powered by either a dc power supply or a 'free-running' rf generator,^{17,18} was used. The anode tube of this source had an inner diameter 4 mm. Again, the plasma gas was supplied to the source *via* a mixing system using four mass flow controllers (Bronkhorst High-Tech B.V.) with different flow ranges: 5, 50, 100, and 500 sccm. Various hydrogen or nitrogen concentrations were again obtained by mixing pure argon (purity 5.0) with a mixture of argon with 2% v/v hydrogen or nitrogen. The pressure was measured by a capacitance diaphragm gauge, Baratron (MKS Instruments, Inc.), with the pressure range up to 100 mbar, connected directly to the body of the glow discharge source. Stainless steel tubing was used for all gas connections. The source was viewed end-on and an image of the cathode was focused with an achromatic quartz fluorite lens on the entrance connector of an optical fibre which transferred the optical signal to the spectrometer. Optical emission measurements were carried out using an Echelle spectrometer ESA 3000 (LLA Instruments GmbH). The spectral range of this instrument is from 200 nm to 1000 nm, the resolution is 5 pm at

200 nm and 27 pm at 600 nm. An intensified CCD was used as a detector.

In both experiments, pure iron (99.5%, Goodfellow) and pure titanium (99.6%, Goodfellow) were used as cathode materials. In addition, a commercial GD-OES instrument GDS500A (LECO) was used for comparative measurements of a pure titanium sample and a TiH₂ layer in a pure argon discharge. The GDS500A instrument is equipped with a standard Grimm-type glow discharge source with 4 mm anode tube and uses a centred sphere spectrometer with CCD array detection, which has a spectral range from 165 to 464 nm and a resolution of 70 pm (310–460 nm), or 85 pm (165–310 nm).¹⁹ The discharge was operated in a dc mode with constant current and constant voltage with dynamic gas flow control.

Measurements of the sputtering rates of iron and titanium at various concentrations of a molecular gas were undertaken by measuring the volume of craters sputtered on the sample surface using a FRT optical depth profilometer (MicroProf) at IFW.²⁰ Samples were sputtered for a defined time in the glow discharge source at constant dc voltage and constant current (700 V and 40 mA) with an 8 mm anode tube in pure argon and in argon–hydrogen or argon–nitrogen mixtures.

Results and discussions

The results presented here are divided into four parts. In the first part, the effect of molecular gases on the sputtering rate of iron and titanium is presented. In the next two parts, changes observed in optical emission spectra of iron and titanium atomic emission lines are described and discussed. Finally, a brief description of the effect of hydrogen on the intensities of iron and titanium ionic lines is given together with a reference to our earlier work published on this topic.

The spectra recorded were analysed in the following way: iron and titanium atomic and ionic lines were unambiguously identified in the spectra and those with sufficiently high intensities and with accessible data on line transitions^{21–23} were selected for further evaluation. As a result of that, sets of iron and titanium atomic and ionic lines were created: 97 lines of Fe I, 82 lines of Fe II, 129 lines of Ti I and 192 lines of Ti II. The intensities of these lines were subsequently measured in spectra recorded in the discharge in pure argon and in argon with small controlled amounts of hydrogen or nitrogen. An intensity ratio for each line was calculated as intensity recorded in the discharge in an argon–hydrogen (or argon–nitrogen) mixture relative to intensity recorded in the pure argon discharge.

It should be noted that in this paper we are considering the general trends rather than the exact effect on individual lines and energy levels, and have therefore not replicated measurements for error estimation. However, the trends obtained in individual experiments at IC London, IFW Dresden and LECO Plzeň are the same, only small differences of quantitative nature were observed.

Sputtering rates

The intensity of the sample emission lines in the analytical glow discharge depends on the number density of atoms of the element which in turn depends on the flux of these atoms into the

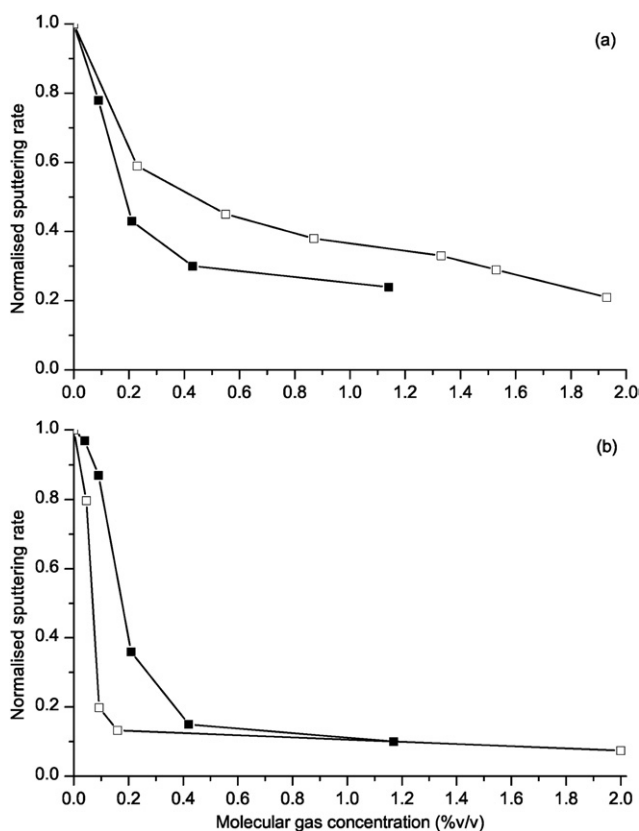


Fig. 1 Normalised sputtering rates for (a) iron and (b) titanium samples as a function of the hydrogen (■) or nitrogen (□) concentration. Results obtained in the discharge at 700 V, 40 mA in 8 mm anode tube.

discharge. This flux can be characterised by the sputtering rate of the sample. Therefore, the sputtering rates of iron and titanium were measured in pure argon and in argon–hydrogen or argon–nitrogen mixtures. The measured sputtering rates were normalised by dividing their values by the one obtained in pure argon. In Fig. 1, plots of the normalised sputtering rates of iron and titanium are shown for both argon–hydrogen and argon–nitrogen mixtures. In all cases, the sputtering decreases with increasing concentration of the molecular gas. The rate at which it drops differs whether iron or titanium is sputtered. In the case of iron, the decrease in the sputtering rate is more gradual than in the case of titanium where there is apparently a sharp drop in the sputtering rate at a certain concentration of a molecular gas. This can be attributed to the fact that titanium has higher reactivity with molecular gases under study compared with the iron sample, and a thin layer of titanium nitride or titanium hydrides is formed at the surface of the titanium sample. These compounds have much lower sputtering rates than metallic titanium. This phenomenon is known from magnetron sputtering techniques as the “target poisoning”. In the results presented in the next sections, the intensities shown are not corrected for the changes in the sputtering rate.

Fe I lines

Throughout this discussion, the effect of the added molecular gas on line intensities is expressed in terms of “intensity ratios”, *i.e.*

the line intensity observed with a mixture of argon and added molecular gas, divided by the line intensity in pure argon. In Fig. 2, intensity ratios for a large number of lines are plotted against the excitation energy of the line (*i.e.* energy of the upper level) for various hydrogen concentrations (0.05, 0.10, 0.50 and 0.8% v/v) under constant current (10 mA) and constant voltage (700 V) mode; the overall gas pressure was therefore different in the individual cases. This mode of operation is very often used in analytical applications because it gives the best consistency of the standard quantification model.²⁴ These data were obtained with 4 mm anode tube at IFW Dresden. Earlier FTS measurements at IC using an 8 mm anode tube showed similar trends.

It is clear from the sputter rate measurements that the sputtering rate of iron decreases quite significantly with hydrogen and this obviously affects the intensity ratios. If hydrogen did not have any effect on the excitation conditions, the plot of the intensity ratios against the excitation energy would yield a straight horizontal line corresponding to the ratio of the sputtering rates measured in argon–hydrogen mixture and in pure argon. As can be seen in Fig. 2, this is not the case and two apparent features can be seen: (a) the intensity ratios of the lines increase with the excitation energy in the range between 3 and 5 eV and above 5.6 eV in some gases, and (b) a prominent selective maximum can be found for some lines with energies between 5.3 and 5.6 eV. Both these features are stronger when lower currents (and therefore lower powers) are used (Fig. 3). The intensity of resonance and near resonance lines may well be affected by self-

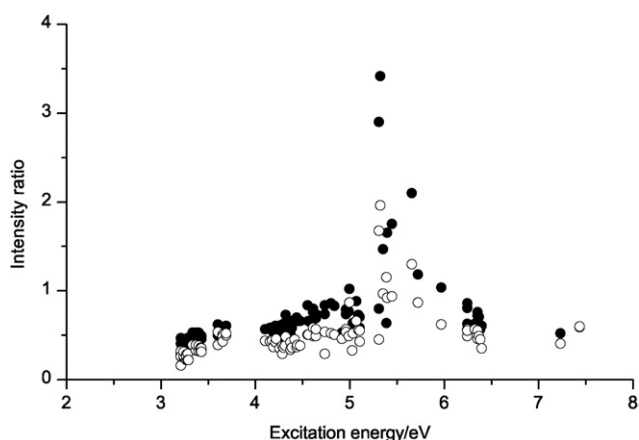


Fig. 3 Intensity ratios of iron atomic lines as a function of their excitation energy for two dc currents: ● 700 V and 10 mA and ○ 700 V and 20 mA. Intensities measured in the discharge in argon with 0.30% v/v hydrogen relative to those measured in pure argon.

absorption and the reduced sputtering rate will decrease this effect for particular lines. However, since the amount of self-absorption depends on the transition probability of the line, such changes will not be related to the value of the upper energy level, and can lead to increased scatter of the points but not affect the overall trend.

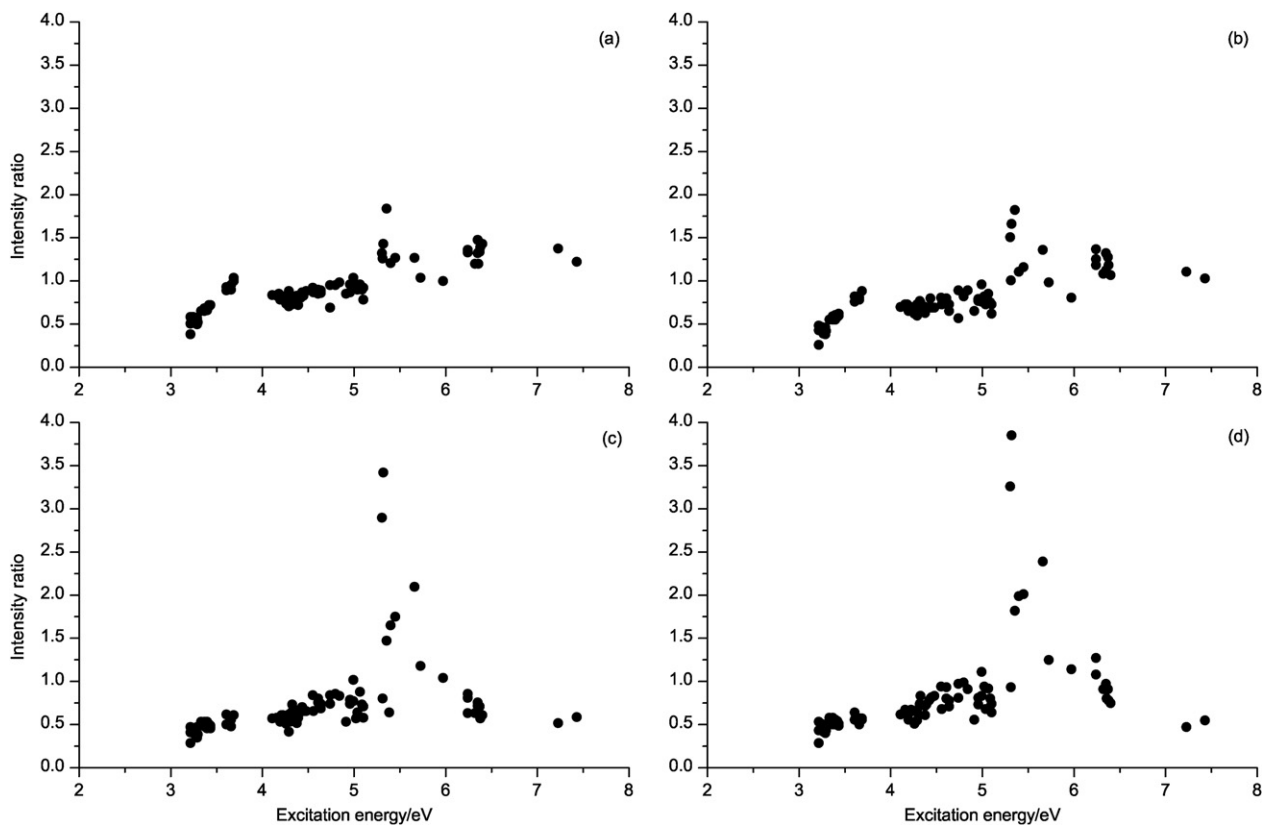


Fig. 2 Intensity ratios of iron atomic lines as a function of their excitation energy: 700 V and 10 mA; intensities measured in the discharge with 4 different hydrogen concentrations relative to those measured in pure argon: (a) Ar + 0.05% v/v H₂, (b) Ar + 0.10% v/v H₂, (c) Ar + 0.50% v/v H₂ and (d) Ar + 0.8% v/v H₂.

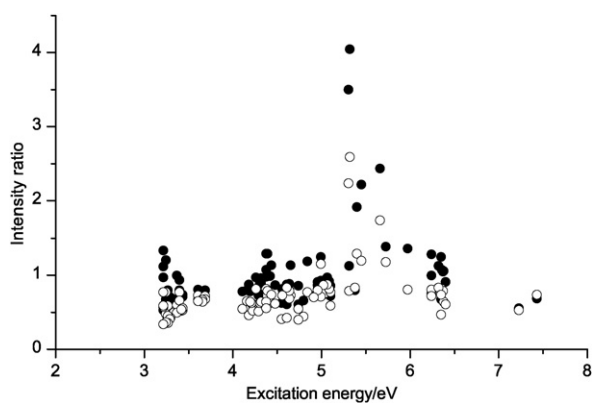


Fig. 4 Intensity ratios of iron atomic lines as a function of their excitation energy for two rf powers: ● 7 W and 700 V and ○ 14 W and 700 V (the effective voltage). Intensities measured in the discharge in argon with 0.50% v/v hydrogen relative to those measured in pure argon.

In Fig. 4, results obtained in the experiments with rf GD at IFW Dresden are shown as the intensity ratios for 0.50% v/v of hydrogen relative to pure argon and for two rf powers. In general, the trends are very similar although there are some individual minor discrepancies for which some further investigation is needed. The effect of hydrogen is again more pronounced at lower power. The rf discharge was operated in a mode with constant effective voltage (700 V) and constant

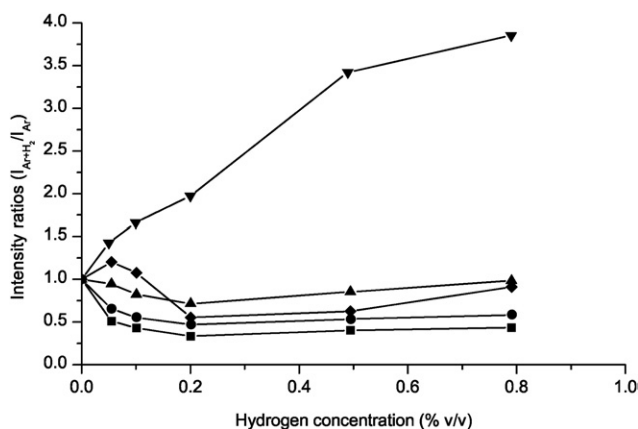


Fig. 5 Intensity ratios of iron atomic lines as a function of hydrogen concentration: ■— Fe I 392.291 nm, 3.211 eV, ●— Fe I 371.994 nm, 3.332 eV, ▲— Fe I 382.782 nm, 4.795 eV, ▼— Fe I 281.329 nm, 5.321 eV and ◆— Fe I 355.492 nm, 6.320 eV. The discharge conditions: 700 V and 10 mA.

power (7 and 14 W). This effect can be very important analytically as, if in an analysis of some very thin layers it is convenient to optimise the discharge parameters so that the sputtering is not so fast, *i.e.* by reducing the current, the effect of hydrogen can be more pronounced.

(a) General trends. Detailed study of the plots shows that there is a difference between the gradient of the intensity ratio increase for the lines with excitation energy between 3 and 4 eV and for the lines with excitation energy between 4 and 5 eV. The gradient of the intensity ratio increase of the lines with excitation energies between 3 and 4 eV decreases with hydrogen concentration whereas for the lines with excitation energies between 4 and 5 eV this gradient increases with hydrogen content. Furthermore, for higher hydrogen concentration the intensity ratios of the lines with excitation energy above 5.6 eV decrease with the excitation energy. If we compare line intensities for *e.g.* 0.05% v/v of hydrogen and pure argon, we can see that the intensity of the lines with excitation energy ~ 3.2 eV is approx. two times lower in the argon–hydrogen discharge than in the case of pure argon, whereas the lines with the excitation energy ~ 3.7 eV are almost unchanged in the presence of hydrogen. The lines with even higher excitation energies (~ 4.1 eV) are again weaker in the presence of hydrogen but by the time we get to the excitation energy of ~ 5 eV, the intensity ratio is getting again close to 1. This increase for this hydrogen content continues also for lines with excitation energy up to ~ 7.5 eV. It has to be stressed that the line intensities without any correction for changes in sputtering rates are compared.

In Fig. 5, the ratios of intensities of several iron atomic lines are plotted against hydrogen concentration: the measured line intensities were divided by the corresponding intensity in pure argon. The lines have been selected so that different excitation energies are covered in the range shown in Fig. 2. Details of transitions of these lines are given in Table 1. It is obvious that different emission lines show different behaviour with increasing hydrogen concentration. The intensities of the three lines with lowest excitation energy (Fe I 392.291 nm, Fe I 371.994 nm and Fe I 382.782 nm) decrease with the hydrogen concentration between 0 and 0.2% v/v after which there is a slight increase. The intensity of the emission lines which is strongly enhanced in the presence of hydrogen (Fe I 281.328 nm) increases rapidly with the hydrogen concentration even at a low hydrogen concentration and is almost as twice as high at 0.2% v/v of hydrogen. The intensity of the line Fe I 355.493 nm goes slightly up at very low hydrogen concentration after which there is a decrease with minimum at about 0.2% v/v followed by a further slow increase. It has to be stressed that the intensities have not been corrected

Table 1 A list of the iron atomic lines shown in Fig. 5 and details of the transitions involved^{21–23}

Wavelength/nm	Lower energy/eV	Upper energy/eV	Configurations		Terms	<i>J</i> lower–upper
			lower–upper			
392.291	0.052	3.211	3d ⁶ 4s ²	3d ⁶ (⁵ D)4s 4p(³ P ^o)	⁵ D– ⁵ D ^o	3–4
371.994	0.000	3.332	3d ⁶ 4s ²	3d ⁶ (⁵ D)4s 4p(³ P ^o)	⁵ D– ⁵ F ^o	4–5
382.782	1.557	4.795	3d ⁷ (⁴ F) 4s	3d ⁷ (⁴ F)4p	³ F– ³ D ^o	3–2
281.329	0.915	5.320	3p ⁶ 3d ⁷ (⁴ F)4s	3d ⁶ (a ³ F)4s 4p(³ P ^o)	³ F– ⁵ G ^o	4–5
355.493	2.833	6.320	3d ⁶ (⁵ D)4s 4p(³ P)	3d ⁶ (⁵ D)4s(⁶ D)4d	⁷ F ^o – ⁷ G	5–6

for the changes in sputtering rates, *i.e.* for the changes in the population of the ground state of iron atom. Hodoroaba *et al.*¹⁴ reported on the intensity of only one iron emission line (Fe I 371.994 nm); this decreased with hydrogen concentration in the range between 0 and 0.1% v/v, the same trend as observed for that line in our experiments.

The patterns in Fig. 2 and 3 suggest there are several groups of lines which are excited by different mechanisms. It has been shown (Bogaerts *et al.*,²⁵ Fig. 5) that atomic lines with lower excitation energies can be excited by collisions with fast heavy particles in the cathode dark space whereas the lines with higher excitation energies are excited mainly by electrons in the negative glow. We have also undertaken several experiments with a modified Grimm-type source which allows viewing the discharge side-on and studying the axial distribution of the line intensities. We observed that for the iron atomic lines with lower excitation energy (<4 eV) the maximum intensity was very close to the cathode with a second intensity peak (smaller than the first one) gradually developing approx. 1–2 mm from the cathode as the excitation energy of the lines increased. The lines with higher excitation energies (4–5 eV), on the other hand, showed their maximum intensity further away from the cathode whereas their intensity near the cathode was gradually decreasing with the excitation energy. Finally, for the lines with even higher excitation energy the intensity maximum close to the cathode was completely missing and only the second maximum in the negative glow was present.

The variation in the intensity ratios with the excitation energy may be linked with the changes in the relative importance of mechanisms responsible for population of individual levels: electron impact excitation, heavy particle excitation, de-excitation from higher levels (both radiative and collision induced). These may be directly due to the presence of hydrogen (change in number density of electrons, argon ions and argon metastables, possibly change in the electron energy distribution function), or may be due to the pressure difference between argon and argon–hydrogen cases. Indeed, in order to keep the electrical parameters constant (a mode with constant current and constant voltage was used), the overall gas pressure had to be increased when hydrogen was added into argon. In Table 2, an overview of the gas pressure variation with hydrogen content is given. It is obvious that when adding 0.05% v/v into argon it is necessary to increase the pressure by 0.7 mbar to keep the electrical parameters constant.

On the other hand, as shown below (see Fig. 6), when nitrogen was used instead of hydrogen, the gradient of the intensity ratios

Table 2 Variations of the gas pressure during the experiments with iron and titanium sample at constant dc electrical parameters

Fe sample at 700 V and 10 mA		Ti sample at 700 V and 20 mA	
H ₂ concentration (% v/v)	Pressure/mbar	H ₂ concentration (% v/v)	Pressure/mbar
0.00	5.83	0.00	6.13
0.05	6.50	0.03	6.77
0.10	6.83	0.14	8.37
0.50	7.00	0.3	9.64
0.8	7.07	2.0	9.64

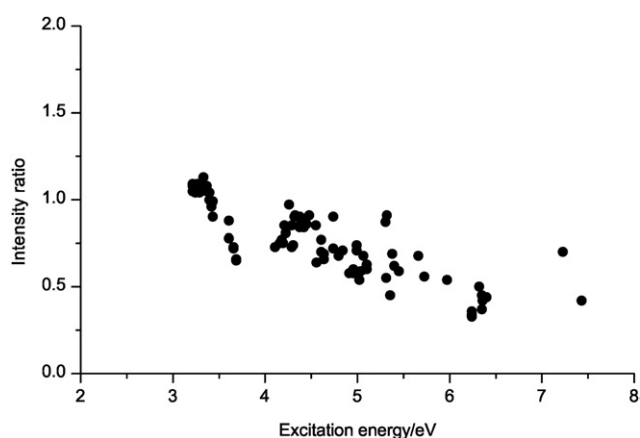


Fig. 6 Intensity ratios of iron atomic lines as a function of their excitation energy: 700 V, 10 mA; intensities measured in the discharge in argon with 0.4% v/v nitrogen relative to those measured in pure argon.

as a function of the excitation energy was almost negligible or even negative. But the overall pressure also had to be increased to maintain constant electrical parameters although the pressure increase was not as large as in the case of hydrogen: 5.69 mbar for pure argon and 6.00 mbar for argon with 0.4% v/v nitrogen. Therefore, one can conclude that the change in the relative importance of the excitation processes is more likely due to the presence of hydrogen rather than due to the pressure increase.

Another possible interpretation of the gradient in the intensity plots might be to consider it as indicating a change in the excitation temperature. Strictly, the excitation temperature is meaningful only if the system is in the local thermodynamic equilibrium (LTE) and it is well known that analytical glow discharges are not in LTE. Nevertheless, we considered this interpretation. If the system were in LTE, intensity of an emission line I_{21} originating from a transition between levels 1 and 2 would be

$$I_{21} = \text{const. } \nu_{12} g_2 A_{21} n_0 e^{-\frac{E_2}{kT}} \quad (1)$$

where the constant includes all the geometric and instrumental factors, ν_{12} is the frequency of the line, g_2 is the statistical weight of the level 2, A_{21} is the Einstein coefficient of spontaneous emission, n_0 is the number density of the atoms in the ground state, E_2 is the excitation energy of the level 2, T is the excitation temperature and k is the Boltzmann constant. If the effect of the molecular gas at a concentration c is to change the excitation temperature from T to T_c , then the logarithm of the intensity ratios can be expressed as

$$\ln \left(\frac{I_{21}^c}{I_{21}} \right) = E_2 \frac{T_c - T}{kT_c T} + \ln \left(\frac{n_0^c}{n_0} \right) \quad (2)$$

where the superscript c refers to the case when the mixed gas is used. It is clear from the expression (2) that the plot $\ln(I_{21}^c/I_{21})$ vs. E should give a straight line with the gradient $(T_c - T)/kT_c T$ and the offset given by the ratio of the number densities in the mixture and in the pure inert gas. This offset would depend on the change in the sputtering rates. The plots in Fig. 2 show that this is not the case, particularly as various sections of the plots behave in different ways. It is clear that hydrogen causes changes

in the relative population of the excited states but in a very complex way.

(b) Selective enhancement of Fe I lines. As the sputtering is reduced when hydrogen is present, changes in the self-absorption may contribute to the enhancement of the lines and this is being investigated further. However, the more significant feature in these plots (Fig. 2) is the strong enhancement of the lines with excitation energies between 5.3 and 5.6 eV. It is obvious that the enhancement is stronger for higher hydrogen concentration but even for 0.05% v/v hydrogen the intensity of these lines is stronger in the argon–hydrogen mixture relative to the pure argon case. A list of lines for which the enhancement has been observed is given in Table 3. In general, there are three main low energy parent configurations in the iron energy structure: $3d^5 4s^2$, $3d^6 4s$ and $3d^7$ (the ground state of iron atom is $3d^6 4s^2 a^5D$). These can give rise to a number of terms and levels whose energy level values overlap. In the lines identified in the spectra of this work, only lines involving energy levels of the latter two parent configurations have been found. The majority of the transitions observed in the spectra involving a level of configuration $3d^6 4s$ are of the sub-configuration $3d^6 ({}^5D)4s$. The 5 lines strongly enhanced in the presence of hydrogen (the first five lines in Table 3) are the only exceptions and have a triplet parent term for their upper level, e.g. Fe I 278.811 nm with $3d^6({}^3H)4s 4p({}^3P^o)$. However, the upper energy level of the last line in Table 3 (Fe I 423.594 nm) has a quintet parent term: $3d^6({}^5D)4s ({}^6D)5s$. Moreover, the lower state of this line is odd and therefore not metastable; hence self-absorption is not a factor for this line.

Such a strong enhancement suggests that some resonant process takes place in the presence of hydrogen at this particular energy but probably this resonant process is more likely for a particular upper configuration. Indeed, the enhancement factor for the Fe I 423.594 nm line is smaller than for the other 5 lines which have their d-electrons of the upper state in a triplet. The fact that this enhancement does not occur only for one particular energy state could be explained by the existence of several low-lying metastable states in the iron energy structure. The ground state of iron is one level of a quintet with the other four levels extending over 0.12 eV. These four levels have the same parity as the ground state, are therefore metastable. The resonance process responsible for the enhancement of this group of lines might involve interaction with the ground state of iron or these low-lying metastable states. However, up to now, no clear explanation of this process has been found.

For comparison, we have studied the effect of nitrogen on the same set of iron atomic lines. In Fig. 6, intensity ratios calculated

from the line intensities recorded in argon with 0.4% v/v nitrogen (6.00 mbar) and in pure argon (5.69 mbar) at 700 V and 10 mA are plotted against their excitation energy. One can see that there is no obvious enhancement for the lines between 5.3 and 5.6 eV. Furthermore, in general the intensity ratios decrease with the excitation energy rather than increasing. The magnitude of the slopes obviously depends on the sputtering rates but this will not affect the *sign* of the gradient. Since there are some changes in the intensity ratios over the range of excitation energies, it can be concluded that nitrogen has some effect on the excitation conditions in the discharge. However, it appears that the effect of hydrogen on iron atomic lines is more significant than the effect of nitrogen.

Ti I lines

A plot of the intensity ratios of titanium atomic lines against their excitation energy is shown in Fig. 7. In this case, argon was mixed with following hydrogen concentrations: 0.03, 0.14, 0.3 and 2.0% v/v. These data were obtained with 4 mm anode tube with the FTS instrument at IC and the subsequent experiments at IFW confirmed the trends. As in the iron case, the mode with constant voltage and constant current was used. In the case of titanium, the results presented in Fig. 7 are for higher current, i.e. 700 V and 20 mA, as opposed to 10 mA used for the iron sample. The reason was that the sputtering rate of titanium drops very significantly with hydrogen which means that the intensities of all titanium lines become relatively weak when hydrogen is present in the discharge. Therefore, in order to be able to study a larger number of titanium emission lines with sufficiently high intensities, it was convenient to use this higher current. Experimental conditions are given in Table 2.

Although the sputtering rate of the titanium decreases with hydrogen content in the discharge, at the very low hydrogen concentration (0.03% v/v) the majority of the intensity ratios are above 1, i.e. most of the lines are stronger when this amount of hydrogen is present in the discharge. At higher hydrogen content, several features can be seen. Firstly, a clear trend is apparent in these plots: the intensity ratios of the lines with the excitation energy between 2 and 3.5 eV are independent of the excitation energy; for the lines with the excitation energy between 3.5 and 5 eV the intensity ratio increases with the excitation energy reaching its maximum at about 4.8 eV; and finally the intensity ratios of the lines with the excitation energy above 5 eV decrease with the excitation energy. Another feature is that all data points in plots (b), (c) and (d) of Fig. 7 are shifted downwards in

Table 3 A list of the iron atomic lines selectively enhanced in the Ar + 0.5% v/v H₂ discharge and details of the transitions involved^{21–23}

Wavelength/nm	Enhancement factor	Lower energy/eV	Upper energy/eV	Configurations		Terms	<i>J</i> lower–upper
				lower–upper			
278.811	2.90	0.859	5.305	$3d^7({}^4F)4s$	$3d^6({}^3H)4s 4p({}^3P^o)$	${}^5F-{}^5G^o$	5–6
281.329	3.42	0.915	5.320	$3p^6 3d^7({}^4F)4s$	$3d^6(a^3F)4s 4p({}^3P^o)$	${}^5F-{}^5G^o$	4–5
273.358	1.65	0.859	5.393	$3d^7({}^4F)4s$	$3d^6(a^3P)4s 4p({}^3P^o)$	${}^5F-{}^5D^o$	5–4
273.548	1.75	0.915	5.446	$3d^7({}^4F)4s$	$3d^6(a^3P)4s 4p({}^3P^o)$	${}^5F-{}^5D^o$	4–3
258.454	2.10	0.859	5.655	$3d^7({}^4F)4s$	$3d^6(a^3F)4s 4p({}^3P^o)$	${}^5F-{}^5G^o$	5–6
423.594	1.47	2.425	5.352	$3d^6({}^5D)4s 4p({}^3P^o)$	$3d^6({}^5D)4s ({}^6D)5s$	${}^7D^o-{}^7D$	4–4

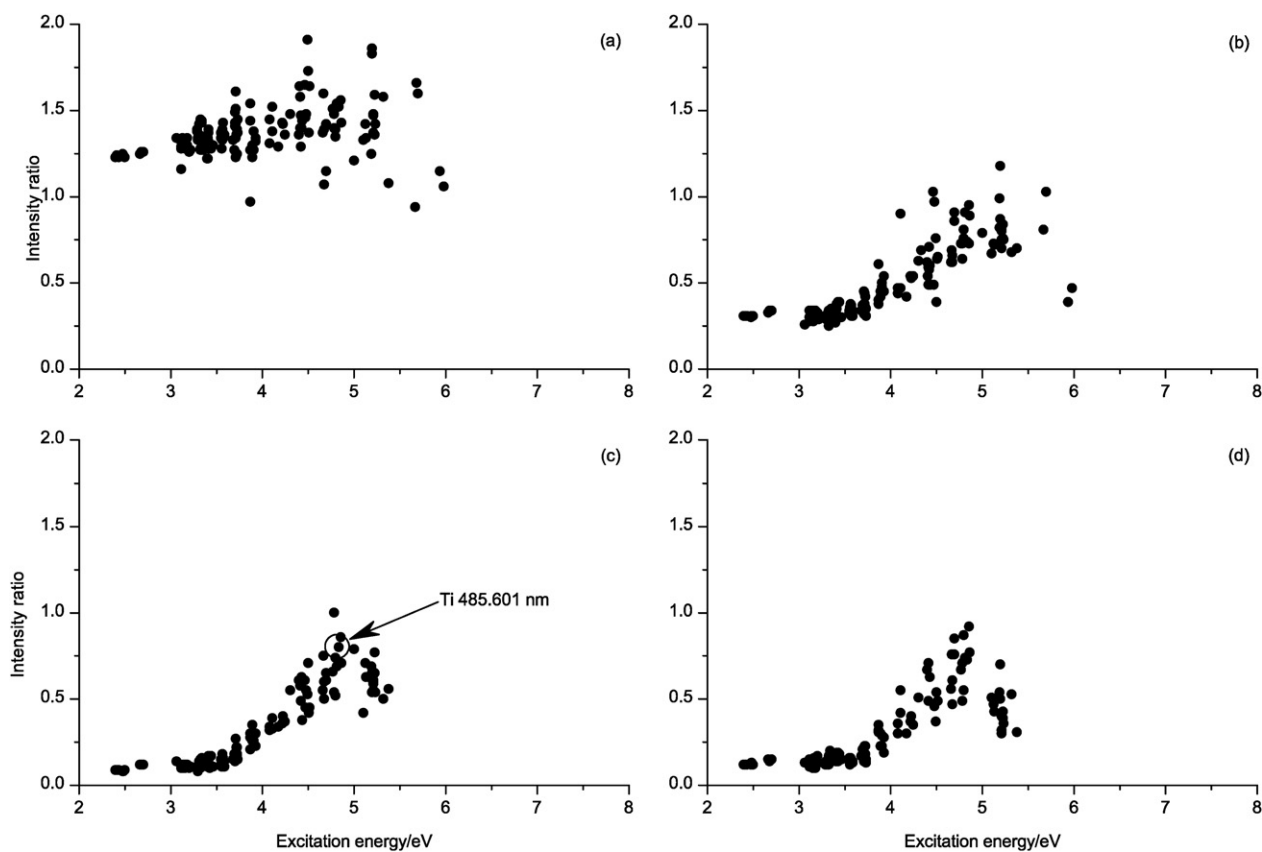


Fig. 7 Intensity ratios of titanium atomic lines as a function of their excitation energy: 700 V and 20 mA; intensities measured in the discharge with 4 different hydrogen concentrations relative to those measured in pure argon: (a) Ar + 0.03% v/v H₂, (b) Ar + 0.14% v/v H₂, (c) Ar + 0.30% v/v H₂ and (d) Ar + 2.0% v/v H₂.

comparison to the 0.03% v/v case which is mainly due to the drop in the sputtering rate of titanium.

The monotonic increase of the intensity ratios with the excitation energy for the lines with the excitation energy between 3.5 and 5 eV suggests that hydrogen also influences the relative population of the excited states in the titanium atom. However, these changes are somewhat different to what has been observed in the iron case. In both cases, the intensity ratios of the lines with the excitation energy above about 4 eV increase with the excitation energy. On the other hand, the lines with the excitation energy below 4 eV which may be excited mainly by the collisions with heavy particles in the cathode dark space, behave differently. In the case of iron, the intensity ratios of these lines also increase with their excitation energy but with different gradient, whereas in the case of titanium, the intensity ratios of these lines hardly change. Another apparent difference is the strong enhancement of the group of iron atomic lines in the range of the excitation energies between 5.3 and 5.6 eV which has not been observed in case of titanium.

In Fig. 8, five titanium emission lines with different excitation energies covered in Fig. 7 have been selected and their intensity ratios plotted against the hydrogen concentration: the line intensities were divided by corresponding values measured in pure argon. Details of transitions of the lines shown in Fig. 8 are given in Table 4. The overall pattern of all lines shown is similar although the relative changes differ: the intensities of the lines

firstly increase with the hydrogen concentration after which there is a sharp decrease. This decrease is certainly linked with the drop in the sputtering rates (*cf.* Fig. 1). There is a marked difference between the behaviour of the Ti I 485.601 nm line which shows one of the highest intensity ratios in Fig. 7(c) (marked in

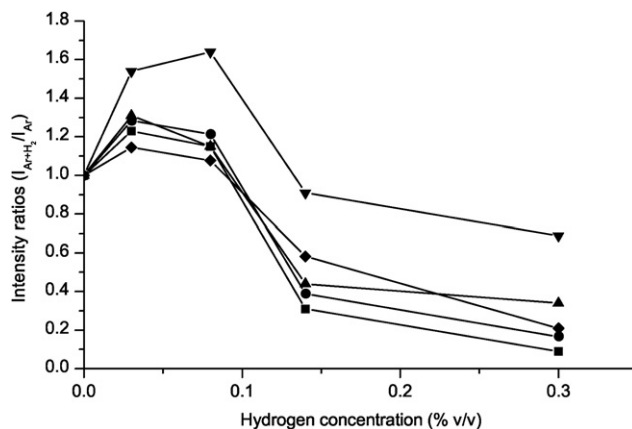


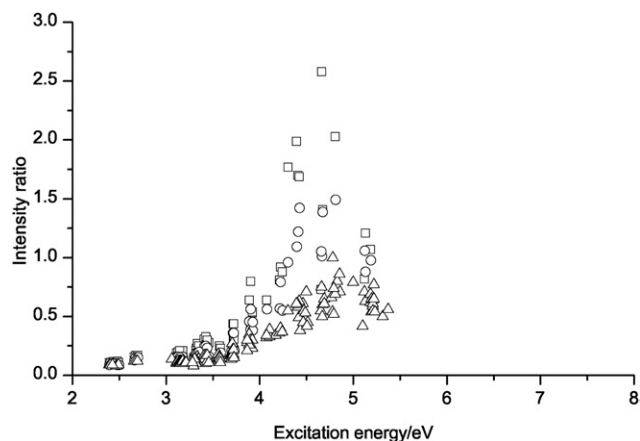
Fig. 8 Intensity ratios of titanium atomic lines as a function of hydrogen concentration: —■— Ti I 506.465 nm, 2.495 eV, —●— Ti I 365.350 nm, 3.441 eV, —▲— Ti I 482.041 nm, 4.074 eV, —▼— Ti I 485.601 nm, 4.808 eV and —◆— Ti I 312.767 nm, 5.930 eV. The discharge conditions: 700 V and 20 mA.

Table 4 A list of the titanium atomic lines shown in Fig. 8 and details of the transitions involved^{21–23}

Wavelength/nm	Lower energy/eV	Upper energy/eV	Configurations		Terms	<i>J</i> lower–upper
			lower–upper			
506.465	0.048	2.495	3d ² 4s ²	3d ² (³ F)4s 4p(³ P ^o)	³ F– ³ D ^o	4–3
365.350	0.048	3.441	3d ² 4s ²	3d ² (³ F)4s 4p(¹ P ^o)	³ F– ³ G ^o	4–5
482.041	1.502	4.074	3d ² 4s ²	3d ² (¹ D)4s 4p(¹ P ^o)	¹ G– ¹ F ^o	4–3
485.601	2.256	4.808	3d ³ (² H)4s	3d ³ (² H)4p	³ H– ³ I ^o	6–7
312.767	1.970	5.930	3d ² (³ F)4s 4p(³ P)	3d ² 4s(⁴ F)5d	³ G ^o – ⁵ H	2–3

Fig. 7(c)) and that of the other lines plotted. In the earlier work by Hodoroaba *et al.*,¹⁴ the intensity of only one titanium emission line (Ti I 365.350 nm, 3.441 eV) was studied in the hydrogen concentration range between 0 and 0.1% v/v. In contrast to our results, they observed a monotonic decrease with the hydrogen concentration in this range with no sign of an increase between 0 and 0.1% v/v. On the other hand, in the work published recently by Obradović *et al.*,¹⁵ where the intensities of several titanium emission lines were studied in the pure argon discharge and in discharges in argon with 0.5% and 3.0% v/v hydrogen, the overall pattern is similar to our results in that the intensities rose and then fell; the maximum intensities were observed when using the 0.5 % v/v H₂ mixture but the concentration yielding the actual maximum is uncertain in view of the very limited number of mixtures investigated. Another important fact which has to be mentioned is that they used an 8 mm diameter anode tube with the current of 18 mA. Furthermore, differences in the experimental setups may also affect the comparison. Although it is not shown in Fig. 8, we have also measured the intensities at 2% v/v of hydrogen (see Fig. 7(d)) but the line intensities are almost unchanged compared to 0.3% v/v.

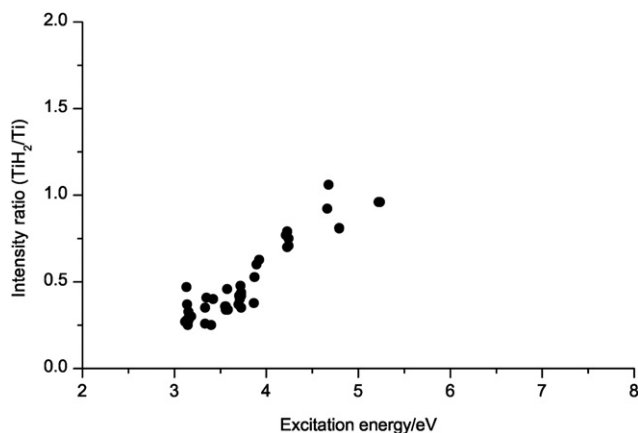
In Fig. 9, a plot of the intensity ratios of the titanium atomic lines as a function of the excitation energy is shown for three different currents and fixed concentration of hydrogen. Similarly to iron, the changes in intensity ratios seem to be more pronounced in case of lower currents in comparison to higher currents. Also, when the same set of lines was evaluated in the

**Fig. 9** Intensity ratios of titanium atomic lines as a function of their excitation energy for three currents: □ 700 V and 10 mA, ○ 700 V and 15 mA and △ 700 V and 20 mA. Intensities measured in the discharge in argon with 0.3% v/v hydrogen relative to those measured in pure argon.

spectra recorded in the discharge with rf excitation, not only the trend was very similar as in the dc case, but also the effect was more pronounced when lower power was used (constant power–constant effective voltage mode).

To compare the situation when hydrogen is added as a molecular gas to the situation when hydrogen enters the discharge from the sample analysed, a TiH₂ layer was sputtered in pure argon and the line intensities recorded were compared to the case when pure titanium was sputtered in pure argon. This experiment was undertaken using the commercial instrument LECO GDS500A, which with medium resolving power and limited spectral range meant that not all lines used in the previous experiments could be studied. In Fig. 10, a plot of the intensity ratios of selected titanium atomic lines as a function of their excitation energy is shown for this experiment at 700 V and 20 mA. It is clear that the increase of the intensity ratios with the excitation energy is similar to the situation when hydrogen is added into argon as a molecular gas.

Furthermore, intensities of the same set of titanium atomic lines measured in pure argon (6.30 mbar) were compared to those recorded in argon with 0.3% v/v nitrogen (8.07 mbar) at 700 V and 20 mA. The result is shown in Fig. 11 as the intensity ratios vs. excitation energy plot. It can be seen that there is no similar trend as in the hydrogen case. But it appears that there is a negative gradient in the intensity ratios in this plot which is similar to what has been observed in case of iron in argon and argon–nitrogen discharge (see above).

**Fig. 10** Intensity ratios of titanium atomic lines as a function of their excitation energy: intensities measured in the argon discharge using TiH₂ sample relative to those measured using a pure titanium sample.

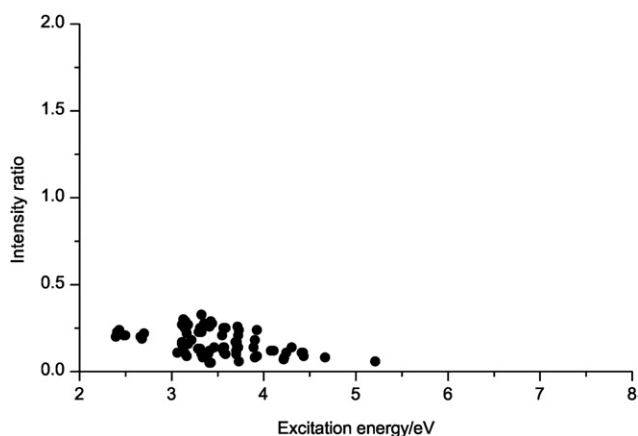


Fig. 11 Intensity ratios of titanium atomic lines as a function of their excitation energy: 700 V and 20 mA; intensities measured in the discharge in argon with 0.3% v/v nitrogen relative to those measured in pure argon.

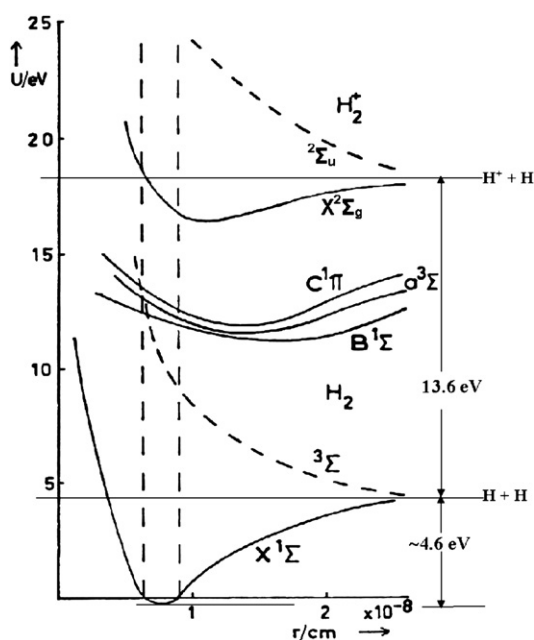
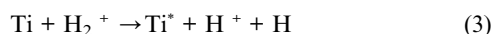


Fig. 12 Potential curves of H_2 molecule; the dissociation energy of H_2 and the ionisation energy of H are also shown.

A possible explanation of rise in intensity ratio with excitation energy up to 5 eV may be collisions between ground state Ti atoms and hydrogen molecular ions, leading to the reaction:



As can be seen from Fig 12, about 4.6 eV are released when hydrogen molecular ions dissociate, but the production of an additional particle in the reaction allows for the conservation both energy and linear momentum without an exact energy resonance. Surplus energy can be converted into the kinetic energy of the particles formed, or indeed extra energy can be supplied from the kinetic energy of the colliding particles. In addition, no data has been located for the cross-sections for this process, but they are likely to be a maximum at about 4.6 eV for

reactions with the Ti atoms in their ground state (an even state). However, the lowest odd Ti I state is at ~ 2 eV, and there are a large number of metastable even states below this energy. They may also be involved in similar reactions, leading to increased intensity ratios up to 6 eV or more.

In the case of nitrogen molecular ions, the energy release on dissociation would be ~ 9.8 eV, well above the normal excitation energy for atomic states, so this process is very unlikely. It is probable that the reaction with hydrogen molecular ions also occurs for Fe atoms, but in this case there appears to be an additional energy-resonant reaction, and to date this has not been identified.

Fe II and Ti II lines

The effect of hydrogen on the ionic lines of iron and titanium has been discussed in a separate paper;¹³ here only a brief summary of the major findings is given. It has been observed that when the intensity ratios of iron ionic lines were plotted against their total excitation energy, the lines with the energy close to 13.6 eV had greater intensity in the presence of hydrogen relative to the pure argon case. A similar effect was subsequently observed for titanium ionic lines. Since this energy (13.6 eV) is the ionisation energy of hydrogen atom, it was concluded that this enhancement of iron and titanium ionic lines is caused by the asymmetric charge transfer collision with hydrogen ion. Also, the intensity of those iron ionic lines which are excited by the asymmetric charge transfer collisions with argon ions are suppressed when hydrogen is present in the discharge.

Conclusions

To date, the only available results covering a large number of spectral lines¹³ have concentrated on *ionic* lines. Results on behaviour of *atomic* emission lines of iron and titanium with small additions of molecular gases have been published only for a limited number of lines.^{14,15} This is the first extensive study of the effect of hydrogen and nitrogen on a large number of atomic lines of these elements; it shows a number of significant features, some of which as yet unexplained. Further studies on these and other related problems are in progress as part of the scientific programme of the EC GLADNET Research Training Network (www.gladnet.eu). With the fast implementation of the instruments with CCD detectors which allow the recording of any selection of emission lines in the available spectral region, it is becoming more important to know the general effects of hydrogen on emission lines of particular elements. It has been shown that both for iron and titanium, there is a correlation between the extent to which individual emission lines are affected by hydrogen and their excitation energy. This represents useful information for further understanding of the processes which take place in the discharge when hydrogen is present. Several iron atomic lines show strong enhancement in the presence of hydrogen and hence they should be avoided in analytical use. Another important feature observed is that the hydrogen effect is more pronounced at lower currents. This has to be kept in mind when optimising the discharge parameters for a particular analytical application, e.g. when it is advisable to use low current if low sputtering rate is required (analysis of a thin film).

Acknowledgements

The authors would like to acknowledge financial support from the EC funded Research Training Network GLADNET, contract no. **MRTN-CT-2006-035459**. P. Šmíd thanks the Royal Society for the award of a one year Royal Society/NATO Fellowship during which the measurements at Imperial College London were undertaken, and the Deutsche Forschungsgemeinschaft (436 TSE 17/7/06) for funding of the experiments carried out at IFW Dresden. P. Šmíd and E. Steers also thank Dr Richard Blackwell-Whitehead from the FTS laboratory at Imperial College London for his technical support and help in their experiments, and Günther Pietzsch for experimental support at IFW Dresden. We also wish to thank Prof. Annemie Bogaerts from University of Antwerp for helpful discussions during which the process suggested in eqn (3) emerged as a possible explanation for the Ti I results and a partial explanation of the Fe I results.

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