

OPEN ACCESS

H α emission in the presence of dust in an Ar-C₂H₂ radio-frequency discharge

To cite this article: I Stefanovic *et al* 2003 *New J. Phys.* **5** 39

View the [article online](#) for updates and enhancements.

You may also like

- [The mechanism of thermally transferred optically stimulated luminescence in quartz](#)
G Adamiec, R M Bailey, X L Wang et al.
- [Blocking of Plasma Stream by Transverse Magnetic Field](#)
Kenji Inoue and Shunsuke Kunieda
- [The Physical Origins of Fast and Slow Components in NBTI Degradation for p-MOS Transistors with SiON Gate Dielectric](#)
Ming-Fu Li, Chen Shen, T Yang et al.

H α emission in the presence of dust in an Ar–C₂H₂ radio-frequency discharge

I Stefanović^{1,2}, E Kovačević¹, J Berndt¹ and J Winter¹

¹ Institute for Experimental Physics II, Ruhr-University, 44780 Bochum, Germany

² Institute of Physics, PO Box 57, 11001 Belgrade, Yugoslavia

E-mail: IS@EP2.RUB.DE

New Journal of Physics **5** (2003) 39.1–39.12 (<http://www.njp.org/>)

Received 5 February 2003

Published 29 April 2003

Abstract. We present the results of time resolved spectroscopy measurements of the H α line of atomic hydrogen in an Ar–C₂H₂ radiofrequency plasma. The presence of the fast (high-energy) and slow (low-energy) components of the hydrogen atoms can be deduced from the Doppler broadening of the H α line. With the appearance of the dust particles, the H α profile became narrower, indicating reduction of the fast component. We discuss several mechanisms for the formation of the fast hydrogen atoms in our plasma. The main cause for the reduction of the hydrogen atom fast component is the plasma change from electropositive to electronegative, decreasing the sheath's width and voltage. The change of plasma conditions coincides with the end of the dust coagulation/agglomeration when the dust particles become multiply negatively charged. We propose here a new experimental technique for detection of the dust coagulation/agglomeration phase.

Contents

1. Introduction	2
2. Experiment	3
3. Results	4
4. Discussion	9
5. Conclusions	11
Acknowledgments	11
References	11

1. Introduction

Investigations of particulate formation in plasmas are of great interest for various branches of science and technology from astrophysics and powder chemistry to electronics and applications for environmental control. The source for dust formation is either the sputtering of the electrode/wafer material (heterogeneous dust growth) or plasma polymerization (homogeneous dust growth). In numerous experiments the dust particles were immersed into the plasma from outside to analyse formation of plasma crystals; references can be found in [1].

The presence of dust particles can influence the plasma conditions to a great extent. Several investigations in silane [2]–[6] as well as hydrocarbon radio-frequency (RF) plasmas [1] showed the changes in electrical properties of the discharge: increase of resistive component of the dissipated power and change in the harmonic frequency spectra. The change in the seventh harmonic voltage amplitude was proposed as a process control parameter for particle growth [7].

The most drastic change in plasma conditions was assigned to the early stage of dust growth, i.e. coagulation or agglomeration [8, 9]. After reaching some critical size the electron loss on the dust exceeds the electron losses to the wall, causing the increase of the local electric field to compensate these losses. As a consequence, the electron concentration decreases and the electron temperature increases. This process is usually called the α – γ' transition.

In a previous paper we reported on some aspects of the dust behaviour in an argon–acetylene gas mixture. It is well known that some discharge conditions and monomer types favour the formation of dust. In the case of hydrocarbon plasmas acetylene compounds have an important role that was recognized by a number of authors [10, 11]. Consequently, acetylene undergoes a polymerization process instantaneously, especially at low flow rate, whereas the polymerization process in other hydrocarbon plasmas often follows the formation of acetylene in the discharge [11]. Polymerization in CH_4 plasmas may be induced, as an example, after transient increase of the power in the discharge [7]. In an $\text{Ar}/\text{C}_2\text{H}_2$ gas mixture we observed the periodic formation and disappearance of the dust particles [12]. By means of ion mass spectroscopy we detected the strong increase of the positive ion count-rates for all relevant ions in the discharge at the very beginning of the particle growth cycle. This increase was correlated with the changes in the reflected electrical power. It had a transient character and cannot be explained in the frame of the α – γ' transition. Also, the timescale for this process is several orders of magnitude larger than reported for the α – γ' transition in silane discharges [8, 9].

In addition to changes in electrical properties, the emission properties of the plasma change [9]. In this paper we measure and analyse the Doppler-broadened Balmer alpha ($\text{H}\alpha$, $\lambda = 656.3$ nm) emission of atomic hydrogen. A number of authors have already investigated this phenomenon in different DC [13]–[17] and RF [13, 18]–[21] plasma sources. The measurements show strongly increased far wings of $\text{H}\alpha$ in pure hydrogen [14, 15] or Ar – H_2 mixtures [16, 17, 21]. The calculated spectral distribution of $\text{H}\alpha$ emission in pure hydrogen in low-temperature plasmas [15] as well as Monte Carlo simulations [22] for high-temperature plasmas showed good agreement with the measured ones, assuming various processes for the formation of fast H atoms.

We have carried out experimental investigations of positive ion production in conjunction with optical emission measurements. During the transient regime we detected a $\text{H}\alpha$ emission with a strong fast-H-atom component. We report here, for the first time, the correlation between the appearance of the fast H atoms and the formation of the dust. After analysing the experimental data we propose a simple, qualitative model to explain the influence of the dust formation on emission profiles of the $\text{H}\alpha$ line.

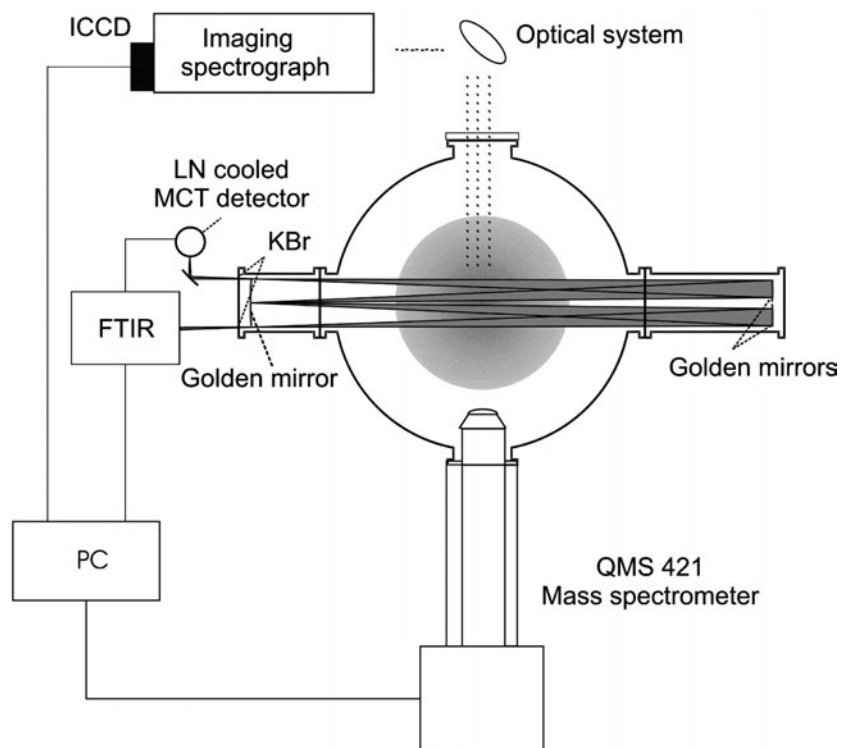


Figure 1. Experimental set-up.

2. Experiment

The investigations were performed in an RF capacitively coupled parallel plate reactor working at 13.56 MHz (figure 1). The electrode system consists of plane, stainless steel electrodes, 30 cm in diameter and separated by 8 cm. The reactor was operated at room temperature, with a mixture of acetylene and argon. The continuous gas flow of 8 sccm for argon and 0.5 sccm for acetylene was controlled with mass flow controllers. The total gas pressure was about 0.1 mbar. The gas residence time was about 1 min. The applied RF power was 10–50 W measured before the match-box.

Infrared (IR) absorption spectroscopy was used to monitor the dust formation dynamics as previously described [12]. The IR beam from the commercial Bruker FTIR spectrometer was directed through KBr windows in the plasma chamber and focused with an off-axis gold mirror onto a liquid-nitrogen-cooled mercury–cadmium–telluride detector (MCT). By means of the multi-pass technique we were able to change the optical path length in the plasma from 0.6 m (two passes through the plasma reactor) to 7.2 m (24 passes).

During the measurement there was a significant deposition of DLC films on the electrodes and discharge chamber walls. To minimize their influence on the nucleation processes we cleaned the discharge chamber after each measurement session by oxygen plasma with high through-flow running continuously for at least half an hour. After this treatment the plasma vessel was pumped for several hours. The residual gas pressure was 6×10^{-6} mbar.

We followed the time evolution of the IR scattering signal as well as different absorption line intensities by measuring full FTIR spectra with the time resolution of 1 min.

For detection of positive ions and neutrals, we used a Balzers plasma process monitor (PPM) 421, which consists of a quadrupole mass spectrometer equipped with ion extraction optics and an ion energy analyser.

The PPM was mounted on the chamber through the side port so that ions were sampled from the side of the plasma. A bellows assembly allowed us to vary the distance between the sampling orifice (100 μm diameter) and the edge of the electrodes. For the measurements presented here it was placed 10 cm outside the electrodes (outside the bulk of the plasma) on the mid-plane between the electrodes and was at floating potential. The time resolved measurements of ion count-rates were made with 1 min resolution time.

The emission spectroscopy measurements were performed by the use of an Acton Research monochromator/spectrograph with a Czerny–Turner mount. The 750 mm focal length monochromator/spectrograph had a reciprocal linear dispersion of 0.74 nm mm⁻¹ with a 1800 gr mm⁻¹ grating. The spectroscopic data were collected by a 1024 \times 256 pixel format, front illuminated ICCD camera from Princeton Instruments. The resolution power of our spectroscopic system was 0.06 nm or 3 pixels with a 10 μm entrance slit width. All data presented here were obtained by observing the emission at 90° from the central axis of the electrodes, i.e. parallel to the electrode surfaces. The inter-electrode space was imaged onto the 3 mm high, 10 μm wide entrance slit by the system of optical mirrors and lenses. The specially designed imaging optics of the spectrograph allowed us to measure spatially resolved optical emission. The signal-to-noise ratio was improved by averaging 50 frames for one spectrum. The exposition time for one frame was 1 s. The spectra were collected in a 1 min interval, enabling us to follow the time development of the spectral emission.

3. Results

Representative spectral profiles of the H α radiation, corresponding to the hydrogen atomic transition from the $n = 3$ to 2 level ($\lambda = 656.3$ nm), emitted from an RF discharge in an Ar/C₂H₂ mixture, are shown in figures 2(a) and (b), respectively. During one measurement we could distinguish between two typical H α profiles. In the first one (figure 2(a)) we recognize a broad component of the Balmer-alpha line due to the strong Doppler broadening ('fast' component—emission from the fast hydrogen atoms) and a narrow component ('slow' component—emission from the low-energy hydrogen atoms). In the second case (figure 2(b)) we observe a large fraction of the slow component and the fast component is present as minor wings only.

From the Doppler width we determined the average kinetic energy of the fast hydrogen atoms to be 30 eV. The energy of the slow hydrogen atoms could only be estimated since most of the profile consists of the spectrograph instrumental broadening.

To gain more insight into the influence of dust on the H α spectral distribution we repeated the same measurements in a pure Ar plasma. The observed H α emission came from the hydrogen adsorbed on the surfaces of the electrodes and walls. The result presented in figure 3 is very similar to the case of the Ar–C₂H₂ plasma without dust. It is obvious that Ar⁺ ions or fast Ar atoms play a significant role in the formation of the fast hydrogen atoms in the vicinity of the electrode surfaces as already stated (see [21] and references therein). The fast H atom emission extended to the plasma bulk, where they were excited in the very efficient collisions with Ar atoms [23].

We have already reported the presence of periodical build-up and disappearance of the dust particles in an Ar–C₂H₂ mixture [12]. In figure 4 we present the time development of the dust

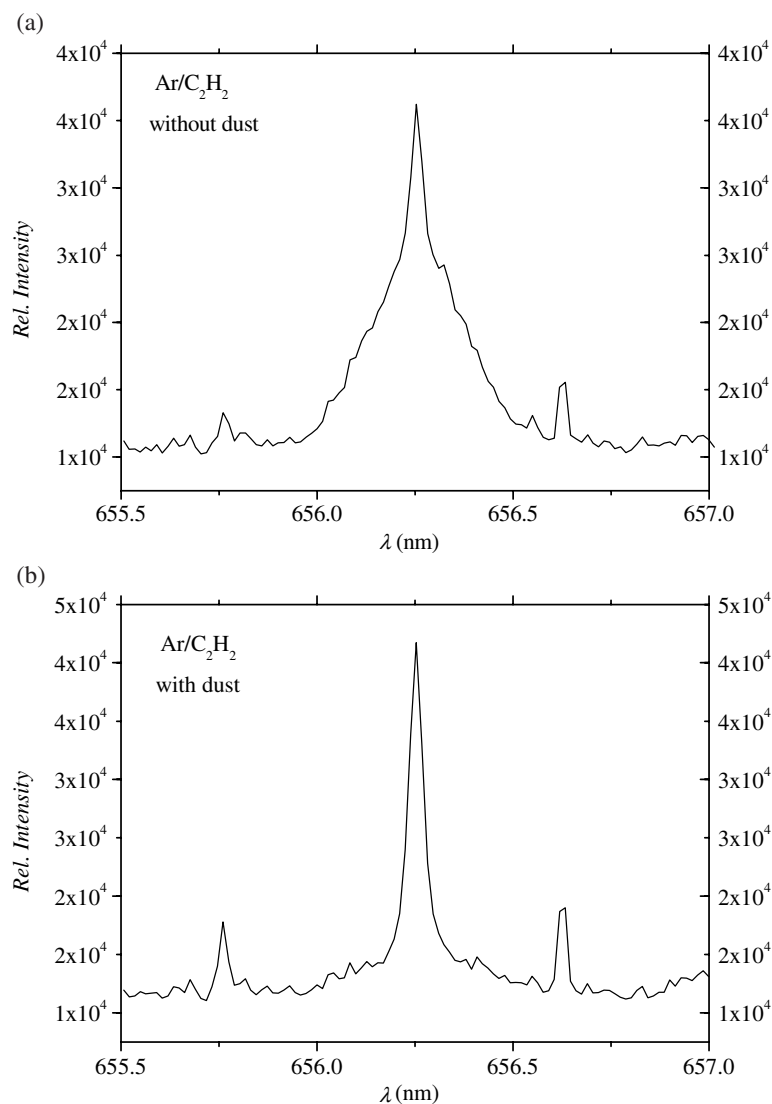


Figure 2. (a) Spectral line distribution of the H α 656.3 nm line in an Ar–C₂H₂ plasma without dust. The discharge power was $P = 50$ W, pressure $p = 0.1$ mbar and the argon to acetylene ratio was Ar/C₂H₂ = 8/0.5 sccm. (b) Spectral line distribution of the H α 656.3 nm line in an Ar–C₂H₂ plasma with the dust present. The plasma parameters were the same as in (a).

scattering FTIR signal together with the Ar⁺ ion dynamics. The C_{2n}H_x⁺ ions follow the same time behaviour but with different amplitudes [12]. The FTIR scattering signal gives us a picture of the particle dynamics in the discharge: the particles are kept inside the plasma by the balance of different forces and grow until some critical size is reached. After reaching the critical size the particles disappear from the line of sight.

Time development of the spectral line intensities was obtained by the integration of the area under the peak. In the case where the H α fast component was present we had to distinguish between two Gaussian profiles: the broader (fast component) and the narrower (slow component)

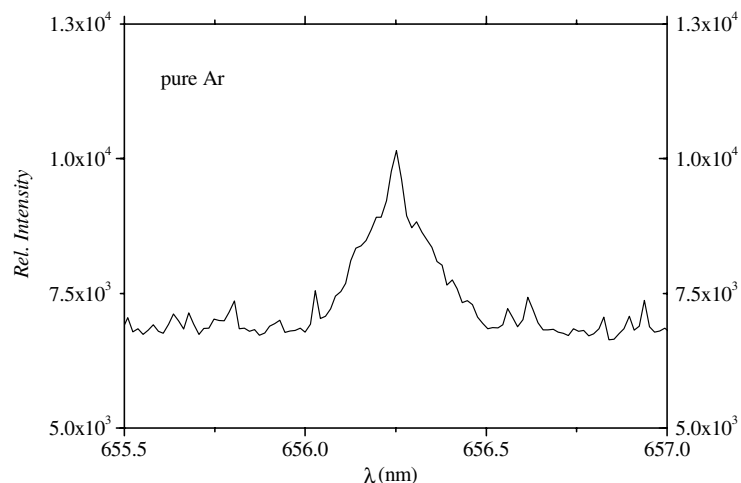


Figure 3. Spectral line distribution of H α 656.3 nm line in pure Ar plasma. All other plasma parameters were the same as in the case of the Ar-C₂H₂ mixture.

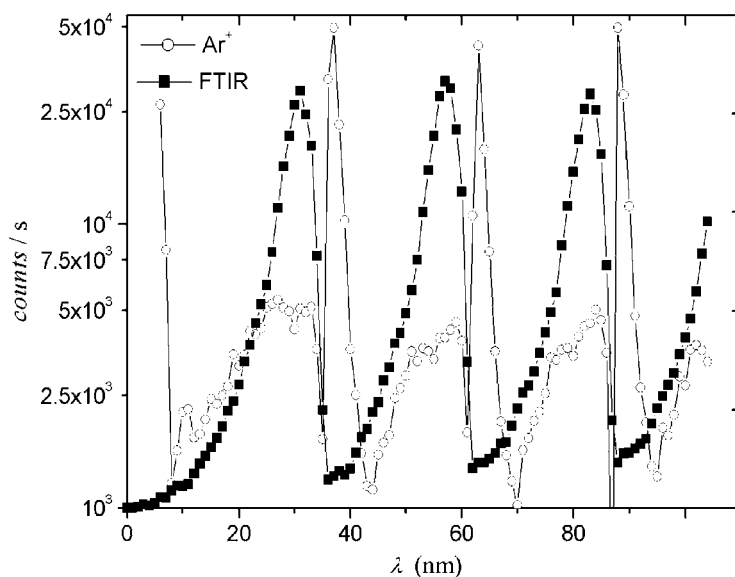


Figure 4. Time development of FTIR scattering intensity (solid squares) and of Ar⁺ ion count rate (open circles).

that was on top of the fast component. In figure 5 we see the periodical growth for the H α slow component and the Ar I 660.45 nm line intensity. This shows the same signature as figure 4, representative of the growth dynamics.

Both line emissions originate from the electron collision excitation and their intensity increase comes from the gradual increase of the electron temperature in the discharge. This effect is known from the silane RF plasmas as a so-called α - γ' transition. It is characterized by the decrease in electron density and increase of the electron temperature to compensate for the large sink of the electrons on the dust particles [8]. The change of the axial light intensity distribution due to α - γ' transition is shown in figure 6. As already reported [9], the spatially

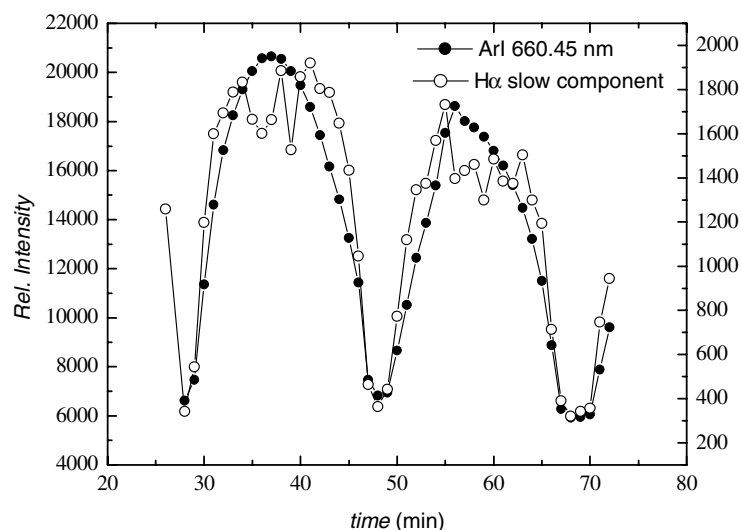


Figure 5. Time development of the integrated line intensity (area under peak) of the H α slow component (open circles) and of the Ar I 660.45 nm spectral line (solid circles).

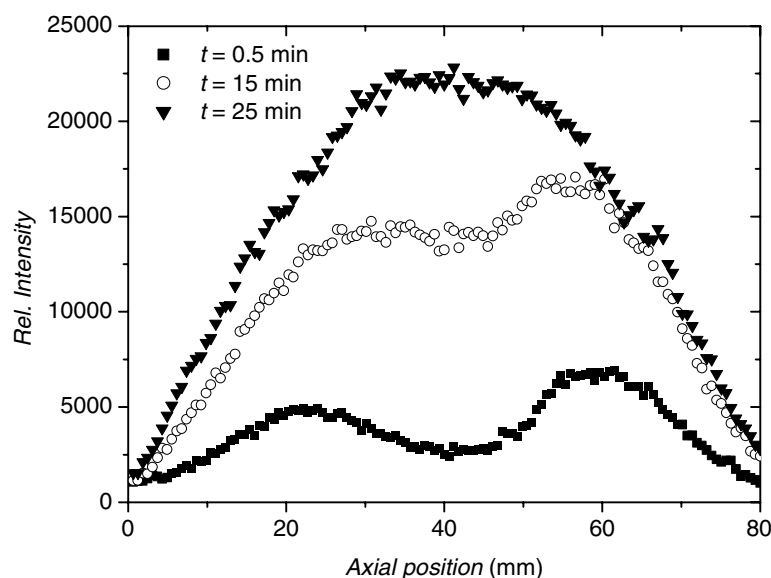


Figure 6. Axial light distribution for three different times after switching on the discharge. Solid squares: 0.5 min (without dust); open circles: 15 min (dust is formed—transient region according to [9]); solid triangles: 25 min (just before the end of the dust growth cycle).

resolved optical emission shows the characteristic transition from collisional ‘wave-riding’ on the sheath boundaries (α regime, solid squares in figure 6) to ‘Joule heating’ in the plasma bulk (γ' regime, solid triangles in figure 6). The characteristic timescale of this process is much larger in our case: about 10 min in comparison to 10 s in the silane case [9].

The same periodicity was detected in the appearance of the fast H α emission component

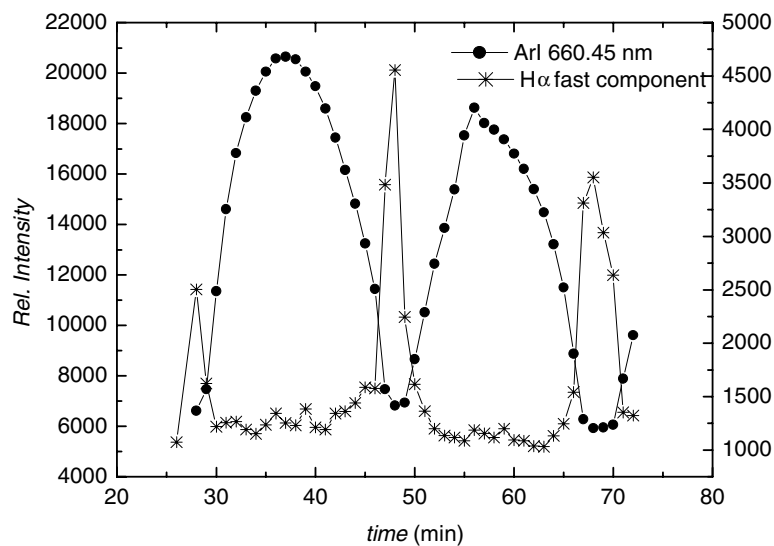


Figure 7. Time development of the integrated intensity (area under peak) of the H α fast component (stars), and the Ar I 660.45 nm line intensity (solid circles).

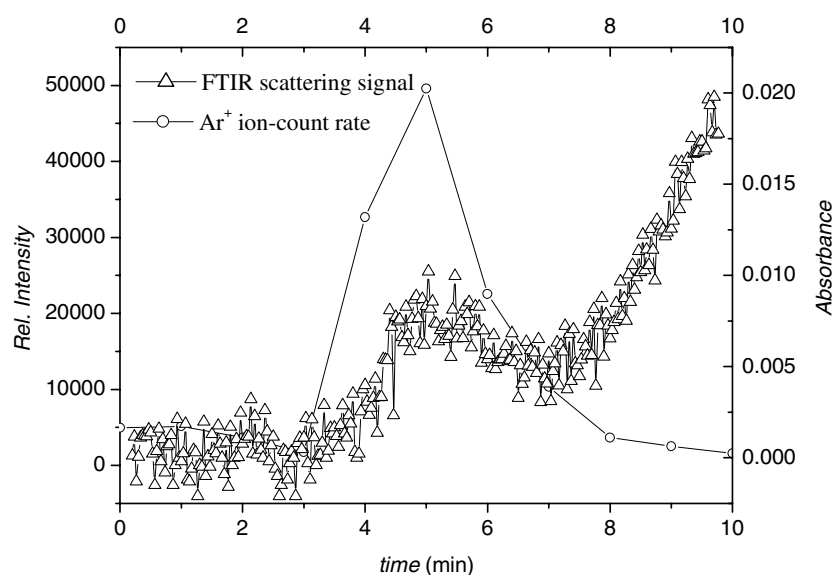


Figure 8. Time development of FTIR dust scattering signal (triangles) and Ar⁺ ion count-rate (open circles) for the first 10 min of the dust growth cycle.

but with the opposite character (figure 7).

Comparing the behaviour of the Ar⁺ ion concentration (figure 4) with the presence of the fast hydrogen atoms (figure 7) we see the strong correlation between them.

Besides the change in concentration of positive ions and fast H atoms there is the change of the scattering FTIR signal, shown in figure 8 on a shorter timescale. The local minimum in the scattering signal is associated with the change in particle size/density and corresponds to the end of the transient regime.

The axial light distribution measurements (figure 6) did not show any transient behaviour that would correspond to the increase of positive ion and fast atom density. The only information gained from the total light intensity distribution is that about the electron collision excitation in the discharge. To obtain information about the dynamics of ions and fast atoms one should concentrate on the $H\alpha$ emission.

4. Discussion

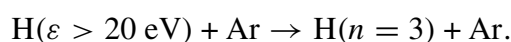
The strong Doppler broadening of $H\alpha$ and other Balmer lines of atomic hydrogen has already been observed by other authors: in pure hydrogen low-pressure DC [13]–[15] and RF discharges [13, 19, 20] or Ar– H_2 DC [16, 17] and RF [21] gas discharges. The same phenomenon was reported in high-temperature plasmas [22]. According to the literature different groups of H atoms contribute to the effect [22].

- (i) According to beam experiments the first group results from the electron-impact excitation of singly bound ($1s\sigma_g$) states of H_2 . Their average energy is about 0.2 eV, that expresses the thermal energy of hydrogen atoms in plasma.
- (ii) The broadened component of approximately 8 eV mean energy results from the dissociative ionization of hydrogen molecules.
- (iii) The third group of atomic hydrogen with high average kinetic energies (> 100 eV) originates from the surface emission or reflection.

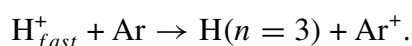
The observed spectral distribution of $H\alpha$ emission in pure hydrogen was explained as the result of collisions between fast H atoms and H_2 [14, 15] due to their large excitation cross sections compared to cross sections for electron and ion collisions [23]. The presence of the fast H atom emission in the plasma bulk suggested that the fast H atoms were reflected from the cathode. The reflection coefficient of the hydrogen atoms was influenced by changing the electrode material [14]. By the proposed model the spectral distribution of the $H\alpha$ line was calculated in agreement with the measured one [15].

The studies of hydrogen excitation in Ar– H_2 mixtures in DC [16, 17] and RF discharges [21] have shown that the presence of argon atoms plays a significant role in producing a large increase of $H\alpha$ emission. It was observed that, in the presence of Ar atoms, the influence of the cathode material became irrelevant [16].

The increase in Doppler-shifted $H\alpha$ emission when argon is added to H_2 can be understood from the high excitation cross section for collisions of fast H atoms with argon atoms [24],

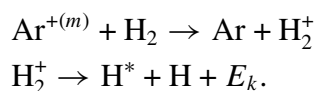


H^+ ions with energies below 100 eV have negligible cross sections for asymmetric charge transfer [24],



Therefore fast H^+ ions cannot be a major direct source of Doppler-broadened emission in the bulk of the plasma [21].

The origin of fast hydrogen atoms is complex. They may be produced in the gas phase initially by charge exchange and neutral–neutral collision. One of the mechanisms proposed was the quasi-resonant charge-transfer process [16, 17]



Fast H atoms may also come from surfaces by dissociation of incident molecular ions, neutralization and scattering of fast ions at the solid surface, ejection of adsorbed hydrogen atoms by ion–surface collisions and reflection of fast neutrals [21].

Our measurements in pure argon discharge (figure 3) show that the $\text{H}\alpha$ profile consists largely of fast hydrogen atoms that dominate the thermal component. This indicates that the primary source of the fast H atoms is collisions of fast Ar or Ar^+ ions with the electrode surfaces. This is in accordance with the assumption that in a pure argon discharge the main source of hydrogen impurities is the hydrogen-contaminated electrode surfaces.

In the case of the Ar– C_2H_2 gas mixture the measured $\text{H}\alpha$ emission profiles were connected to the appearance of the dust particles in the plasma (figures 2(a) and (b)). According to figures 4 and 7 the presence of fast hydrogen atoms is strongly correlated with the presence of Ar^+ ions. The simple explanation for this effect may be as follows: after reaching the critical radius the dust particles disappear from the plasma volume and a new growth process immediately starts [9]. At the same time the increase of all positive ions is detected, in particular of the Ar^+ ion flux (about 50 times larger). H atoms are desorbed kinetically (ion-induced desorption) or reflected from the electrode and reach the plasma bulk experiencing many elastic collisions which would tend to produce a nearly isotropic distribution of velocities in the bulk of the discharge [21]. This is the reason why we could measure the large number of fast hydrogen atoms in the electrode regions as well as in the middle of the discharge.

The increase of the fast $\text{H}\alpha$ line component has a transient character, the same as the increase of all positive ions in the discharge [12]. The end of the transient phase corresponds to the local minimum on the time dependent FTIR scattering signal, presented in figure 8. We suggest that this reversal in scattering signal is a sign of the end of the coagulation/agglomeration process. From this moment on the particles are multiply charged and start to be a considerable ion/electron sink, reducing the ion and electron density [2]–[4, 6]. This is one of the reasons for the strong decrease of the Ar^+ ion density.

The appearance of the negatively charged dust particles dramatically changes the discharge character from electropositive to electronegative, as already discussed by several authors [25]–[28]. The increase of the electronegative character of the discharge causes the narrowing of the plasma sheath and the increase of the electric field in the discharge volume [25, 26]. This reduces the primary source of fast hydrogen atoms as well as other ions.

In the rest of the growth cycle the integrated line intensity of the slow $\text{H}\alpha$ line component behaves as the intensity of Ar I lines (figure 5) following the increase of electron excitation collisions and/or electric field in the discharge volume. The spatial (figure 6) and temporal (figure 5) variation of these intensities is thus correlated with the spatial–temporal variation in the density of electrons with energies that exceed those required for excitation. The increase of the electron excitation and ionization collisions is the consequence of the increase of electron temperature, already explained as the α – γ' transition [4, 6, 9].

5. Conclusions

The spectral line profile of H α radiation from a dust-producing Ar/C₂H₂ plasma shows two different shapes (one with a great amount of the fast component and one with a dominant slow component), strongly dependent on the appearance and growth of the dust particles.

The periodicity in the dust build-up/disappearance process, characteristic for the Ar/C₂H₂ RF discharges, consequently leads to a concomitant periodicity in the fast H atom and Ar⁺ ion appearance. However, the temporal evolution of the fast H α component shows a big difference compared to other measured spectral line profiles (rapid peaking at the beginning of the growth cycle).

Furthermore, the peaking of the fast H α line component has transient character, exactly the same as the strong peaking of the concentrations of all positive ions in the discharge [12], both corresponding to the behaviour of the scattered FTIR signal (first local maximum/minimum, figure 8). These rapid/drastring changes are correlated with the coagulation process in the plasma. The build-up of the multiply charged dust changes the plasma character from electropositive to electronegative, narrowing the sheath width and lowering the sheath potential. This explains the drop in the Ar⁺ ion count rate and reduction of the H α fast component.

In the rest of the dust growth cycle the power deposition in the plasma is volume dominated due to the increase of the electric field in the volume compensating for the attachment losses of ions and electrons. This process is similar to the α - γ' transition described for silane plasmas but with the larger timescale [4, 6, 9].

The measurements of the H α line shape may thus be used to determine the point of the particle coagulation/agglomeration. This could be a complementary technique to the laser light scattering which loses its sensitivity with decreasing particle radius.

Acknowledgments

One of the authors (IS) is grateful to Z Lj Petrović for many fruitful discussions. This work was supported by DFG (project B1, SFB 591).

References

- [1] Bouchoule A (ed) 1999 *Dusty Plasmas* (New York: Wiley)
- [2] Boeuf J P 1992 *Phys. Rev. A* **46** 7910
- [3] Belenguer Ph *et al* 1992 *Phys. Rev. A* **46** 7923
- [4] Boeuf J P and Belenguer Ph 1992 *J. Appl. Phys.* **71** 4751
- [5] Kortshagen U and Bhandarkar U 1999 *Phys. Rev. E* **60** 887
- [6] Fridman A A, Boufendi L, Hbid T, Potapkin B V and Bouchoule A 1996 *J. Appl. Phys.* **79** 1303
- [7] Hong S H, Berndt J and Winter J 2003 *Plasma Sources Sci. Technol.* **12** 46
- [8] Bouchoule A and Boufendi L 1993 *Plasma Sources Sci. Technol.* **2** 204
- [9] Perrin J, Böhm Ch, Etemadi R and Lioret A 1994 *Plasma Sources Sci. Technol.* **3** 252
- [10] See for example
 Kobayashi H, Bell A T and Shen M 1974 *Macromolecules* **7** 277
 Tibbitt J M, Jensen R, Bell A T and Shen M 1977 *Macromolecules* **10** 647
 Stoykov S, Eggs C and Kortshagen U 2001 *J. Phys. D: Appl. Phys.* **34** 2160
- [11] Deschaneux Ch, Affolter A, Magni D, Hollenstein Ch and Fayet P 1999 *J. Phys. D: Appl. Phys.* **32** 1876
- [12] Kovačević E, Stefanović I, Berndt J and Winter J 2003 *J. Appl. Phys.* **93** 2924
- [13] Vrhovac S B, Radovanov S B, Bzenić S A, Petrović Z Lj and Jelenković B M 1991 *Chem. Phys.* **153** 233

- [14] Petrović Z Lj and Phelps A V 1991 *Proc. Int. Seminar on Reactive Plasmas (Nagoya)* paper E-3, p 351
- [15] Petrović Z Lj, Jelenković B M and Phelps A V 1992 *Phys. Rev. Lett.* **68** 325
- [16] Kuraica M and Konjević N 1992 *Phys. Rev. A* **46** 4429
- [17] Kuraica M, Konjević N and Platiša M 1992 *Spectrochim. Acta B* **47** 1173
- [18] Baravian G, Chouan Y, Ricard A and Sultan G 1987 *J. Appl. Phys.* **61** 5249
- [19] Djurović S and Roberts J R 1991 *J. Appl. Phys.* **70** 82
- [20] Radovanov S B, Dzierżęga K, Roberts J R and Olthoff J K 1995 *Appl. Phys. Lett.* **66** 2637
- [21] Radovanov S B, Olthoff J K, Van Brunt J and Djurović S 1995 *J. Appl. Phys.* **78** 746
- [22] Reiter D, Bogen P and Samm U 1992 *J. Nucl. Mater.* **196–198** 1059
- [23] Phelps A V 1990 *J. Chem. Phys. Ref. Data* **19** 653
- [24] Phelps A V 1992 *J. Chem. Phys. Ref. Data* **21** 883
- [25] Gottscho R A 1987 *Phys. Rev. A* **36** 2233
- [26] Boeuf J P 1987 *Phys. Rev. A* **36** 2782
- [27] Bletzinger P 1990 *J. Appl. Phys.* **67** 130
- [28] Kakuta S, Tochikubo F, Petrović Z Lj and Makabe T 1993 *J. Appl. Phys.* **74** 4923