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ENERGY DISTRIBUTION OF HYDROGEN IONS IN CAPACITIVELY COUPLED LOW PRESSURE DISCHARGE[1]

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The H_3^+, H_2^+ and H^+ ion energy distributions (IEDs) were recorded in the 13.56 MHz hydrogen glow discharges with the energy dispersive quadrupole mass spectrometer (PPM 421) horizontally mounted between the discharge electrodes. The discharge was capacitively coupled with an asymmetric arrangement. The measurements were spatially resolved along the discharge axis, i.e. perpendicular to the electrodes, and reflected the ion flux to the grounded PPM extraction orifice 15 mm aside the electrodes. The IEDs of H_3^+ and H^+ revealed a saddle structure that was suppressed by an effect of collisions in case of H_2^+. The H^+ with energies up to 10 eV higher than the maximum energy of the saddle structure were observed and explained by a dissociative ionization of H_2. We proved an appreciable impedance of the plasma glow region from the width changes of the saddle structure. The effect of pressure and rf power on the IEDs was studied for a fixed position at the glow region.

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1 Introduction

Discharges in hydrogen are used for cleaning, reduction, treatment of semiconductors, plasma deposition etc. For many applications the amount and energy of ions play a crucial role because they represent highly reactive species with relatively high energies. The most abundant ions in hydrogen discharges are H_3^+, H_2^+ and H^+ but also heavier clusters up to H_{11}^+ were observed [1].

The energy distribution of ions (IED) bombarding solid surfaces in the rf discharges is usually measured at the grounded or rf electrode. The IEDs of argon ions perpendicularly to the discharge axis, i.e. in between the discharge electrodes, were presented by Olthoff *et al.* in [2]. Here, they discussed a dependence of the IED shape on the position of the measurement point with respect to the active region of the discharge, i.e. horizontal distance of the analyzer orifice. In the present paper the horizontal distance was fixed and spatially resolved measurements along the discharge axis were carried out in order to study a discharge structure.

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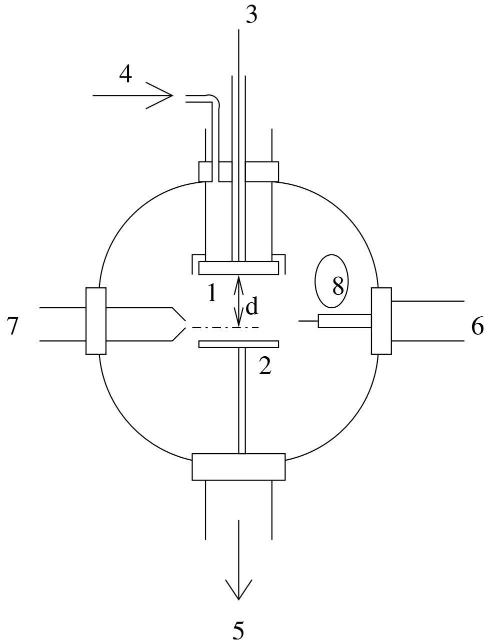

Fig. 1. The schema of the experimenal apparatus: 1. rf electrode, 2. grounded electrode, 3. rf power input line, 4. feeding of gases, 5. towards vacuum pumps, 6. horizontally movable Langmuir probe, 7. PPM 421 devise, 8. quartz window for emission spectroscopy. Vertical distance between the rf electrode and extraction orifice of the PPM 421 is denoted d.

2 Experimental

The experiments were carried out in a spherical (i.d. 250 mm) stainless steel reactor with two horizontally mounted, parallel, stainless steel electrodes of 80 mm in the diameter. The upper electrode, embedded in a grounded ring, was driven at the frequency of 13.56 MHz. The bottom electrode was grounded. Their distance was 40 mm. The IEDs of hydrogen ions were measured as a function of rf power and vertical distance from the rf electrode for the hydrogen flow rate of 6 sccm, i.e. 2.5 Pa. Additionally, the effect of pressure on the IED was studied for constant rf power of 30 W and vertical distance 31 mm. In this case the pressure varied in the range 1.65–3.5 Pa changing the hydrogen flow rate from 4 to 9.5 sccm. At the typical conditions, rf power of 30 W and pressure of 2.5 Pa, the dc self-bias on the powered electrode was -150 V demonstrating an asymmetric nature of the discharge due to grounded reactor parts. The IEDs were measured by Plasma Processes Monitor PPM 421 (Balzers) consisting of an entry ion optics, a cylindrical mirror energy analyzer, a quadrupole mass filter and a secondary electron multiplier. The PPM was mounted parallelly to the electrodes and its grounded extraction hood was 15 mm aside the electrode edges. The schema of the experimental apparatus is shown in the Fig. 1.

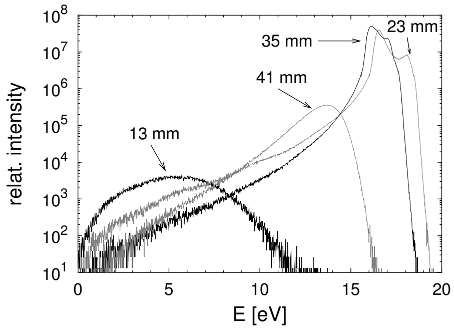

Fig. 2. IED of $\mathbf{H}_3^+$ in different vertical distances from the rf electrode for 2.5 Pa and 30 W.

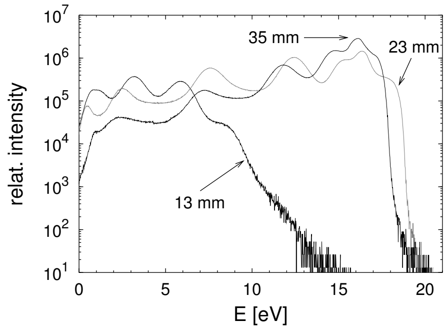

Fig. 3. IED of $\mathbf{H}_2^+$ in different vertical distances from the rf electrode for 2.5 Pa and 30 W.

3 Results and Discussion

In order to estimate the energy dependence of the PPM sensitivity the transmission of the entry ion optics had to be calculated. At first we calculated critical angles for ions impinging on an orifice in the extraction hood. The critical angle is defined as the largest angle between the ion velocity and the optical axis of the entry optics enabling the ion to go through the entry optics into the energy analyzer. Ions impinging at angles larger than the critical angle cannot reach the energy analyzer and are captured by some of the electrodes in the entry optics. The critical angle depends on the kinetic energy of the ion. The transmission of the entry ion optics can be evaluated integrating the ion angle distribution (IAD) up to the critical angle. Unfortunately, the IADs are not known. In order to find an approximate transmission function we supposed that the ion velocity component perpendicular to the optical axis has Maxwell distribution. The ion temperature in the distribution was assumed to be 410 K equal to the rotational temperature of neutral gas measured by optical emission spectroscopy. This assumption was based on the fact that the kinetic energy of ions in the glow region of rf discharges is comparable to the temperature of neutral gas because the ion plasma frequency is well below the rf frequency. The low value of the ion plasma frequency caused by the low ion density (approximately 10^7 cm^{-3}) was confirmed by the Langmuir probe measurements. The results obtained by the optical emission spectroscopy and the Langmuir probe measurements will be published in a forthcoming paper.

The calculated transmission function was in the whole measured energy range higher than 94 % so that the measured IEDs were not significantly distorted by the PPM. It is worth to notice that the assumptions above can lead to an underestimation of the perpendicular velocities and consequently to an overestimation of the transmission function. Nevertheless, we corrected the measured IEDs by means of the calculated transmission function.

The dominating ions in the discharge were H_3^+ produced mainly by the reaction

$$\mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H}. \tag{1}$$

Their distribution function was relatively simple with a saddle structure and a tail rapidly decreasing towards lower energies (see Fig. 2). The IED of H_2^+ had many peaks in the whole spectrum

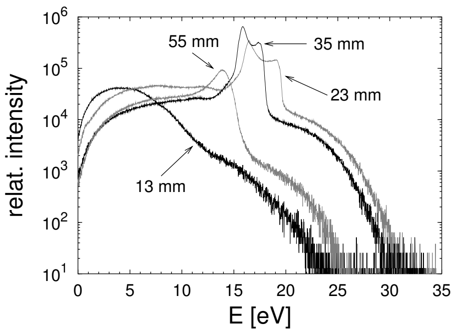

Fig. 4. IED of $\mathbf{H}^+$ in different vertical distances from the rf electrode for 2.5 Pa and 30 W.

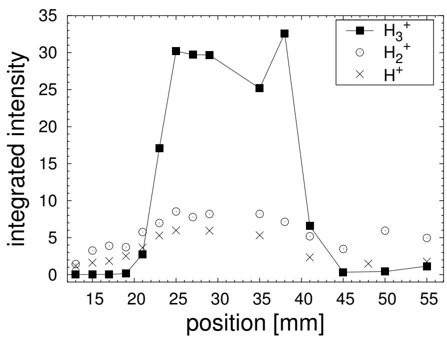

Fig. 5. Integrals of the IEDs of H^+, H_2^+ and H_3^+ in different vertical distances from the rf electrode. 40 mm is the position of the grounded electrode.

so that the saddle structure could not be exactly distinguished (see Fig. 3). This complicated structure resulted from a charge transfer reaction having a relatively large cross section [3, 4]. The ion with the lowest concentration was H^+. Its distribution function had a well developed broad saddle structure (see Fig. 4) caused by its low mass [5]. No clusters with more than three hydrogen atoms were observed.

It is interesting to discuss an origin of the high-energy tail in the H^+ energy distribution. We can see from Fig. 4 that some H^+ ions have kinetic energy more than 10 eV higher than the high-energy part of the saddle structure. The presence of the H^+ ions with such a high energy can be explained by a dissociative ionization of the H_2 molecules by electron impact via the repulsive ${}^2\Sigma_u^+$ state of the H_2^+ [6]. This process requires electrons with energy over 30 eV and produces H^+ ions with the energy observed.

The IEDs of the H_3^+, H_2^+ and H^+ ions for different vertical distances from the rf electrodes are shown in Fig. 2, 3 and 4, respectively. Their concentrations decreased significantly in the above given ion sequence. Therefore the IEDs had to be measured with different voltages on the secondary electron multiplier and the absolute values in the figures cannot be compared. The integrals of the IEDs in dependence on the distance from the rf electrode are shown in Fig. 5. The structure of the IEDs and their integrals did not change strongly while moving the PPM extraction orifice along the glow region (approximate position range 23–38 mm). The width of the saddle structure was slightly reduced when the PPM moved towards the grounded electrode. This is a result of decreasing rf voltage amplitude when moving from the sheath edge at the rf electrode to the grounded one. Therefore, we can see that the impedance of the glow region is not negligible.

The IEDs and their integrals exhibited strong variations as concern the spatial changes along the sheath at the rf electrode (see Fig. 2–5 for the position below 23 mm). The IED integrals outside the glow region were rapidly decreasing, especially for H_3^+. This can be explained by a decrease of the ion concentration in the sheath as well as by the fact that the positive ions are attracted rather to the rf electrode than to the grounded extraction hood. The dip of the H_3^+ IED integrals in the discharge centre seems to be only a random measurement error. The mean ion

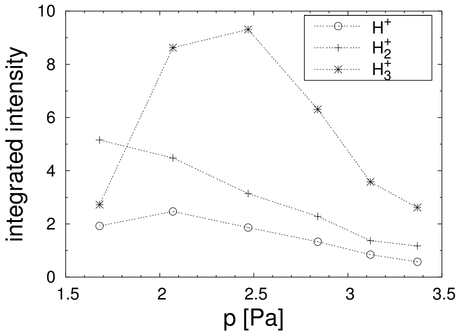

Fig. 6. Pressure dependence of the IED integrals measured at the glow region in the vertical distance from the powered electrode of 31 mm. The rf power was 30 W.

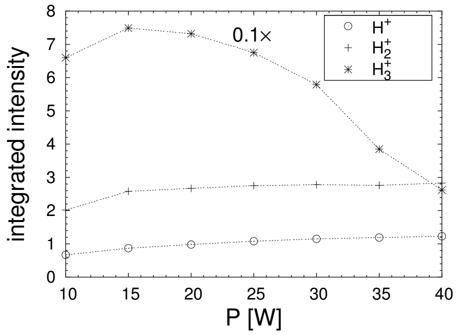

Fig. 7. Dependences of the IED integrals on rf power at 1.65 Pa. In order to compare all three ions in the same graph the values for H_3^+ were 10× decreased. The H^+ IED was measured with different voltage on the multiplier.

energy along the sheath was relatively low because the detected ions are coming from the low potential region and can not get high energy during their flight to the grounded extraction hood. Additionally, the fast ions accelerated by the dc electric field in the sheath and scatered towards the PPM lost a part of their kinetic energy by collisions.

Compared to the rf electrode the sheath at the grounded electrode was very thin due to discharge asymmetry mentioned above. Therefore, the spatially resolved IEDs along this sheath could not be measured. The IEDs integrals and simultaneously the mean ion energy decreased at the position close to the grounded electrode. A detectable concentration of the ions was detected even below the grounded electrode in agreement with Ref. [7].

The dependence of the IED integrals on the pressure is in Fig. 6. The IED integrals for H^+ and H_2^+ decreased with increasing pressure. The IED integral for H_3^+ is also decreasing at the pressures above 2.5 Pa whereas an opposite behavior was observed below. Since the H_3^+ ions are created by collisions their concentration decreases when the collisional frequency of the H_2^+ with H_2 is significantly decreased. We expect the decrease of the IED integrals with increasing pressure being caused by the decrease of the electron temperature, but this assumption has to be confirmed by Langmuir probe measurements.

Dependences of the IED integrals on the rf power measured at the pressure of 2.5 Pa and the vertical distance 31 mm from the rf electrode, i.e. in the glow region, are shown in Fig. 7. The IED integrals for H_2^+ and H^+ did not depend strongly on the power. The H_3^+ IED integral, however, decreased when the power was increased. We intend to carry out measurements with a Langmuir probe providing information about electrons and plasma potential in order to clarify possible reasons for the observed decrease of the H_3^+ IED integral.

4 Conclusion

The H_3^+, H_2^+ and H^+ IEDs spatially resolved along the discharge axis, i.e. perpendicular to the electrodes, were recorded in the rf hydrogen glow discharges at the grounded PPM extraction orifice 15 mm aside the electrodes. H_3^+ was the dominating ion. The IEDs of H_3^+ and H^+ ions revealed a saddle structure that was suppressed by an effect of collisions in case of H_2^+. The H^+ with energies up to 10 eV higher than the maximum energy of the saddle structure were observed and explained by a dissociative ionization of H_2 via the repulsive $^2\Sigma_u^+$ state of the H_2^+. The amount of the detected ions and their energy distributions were almost independent on the measurement position along the plasma glow region. Little changes in the width of the saddle structure along the glow region were observed. This indicated that the glow region impedance should not be neglected. Contrary to the behavior of the IEDs in the glow region the amount and the mean energy of ions detected along the sheaths decreased rapidly. However, even below the grounded electrode a certain amount of all three above mentioned hydrogen ions were detected. The effect of pressure and rf power on the IEDs was studied for a fixed position at the glow region.

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