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## Increased atomic hydrogen flux from a cascaded arc plasma source by changing the nozzle geometry

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A very high flux of hydrogen atoms with energies in the eV range has been obtained by using a thermal plasma source and by optimization of the nozzle exit geometry. It proves that the flux of hydrogen atoms emerging from a cascaded arc plasma source depends strongly on the geometry of the nozzle. By decreasing the nozzle length by a factor 2, the atomic hydrogen flux is increased by a factor of 13, and a further increase of a factor of 2.5 can be obtained by increasing the nozzle diameter. The resulting atomic hydrogen flux is  $1.2 \times 10^{21} \text{ s}^{-1}$ , corresponding to a dissociation degree of over 30%. It is argued that the main loss channel for atomic hydrogen is surface recombination, and that by using nozzle geometries that reduce the surface loss, the atomic flux is increased. © 2005 American Institute of Physics. [DOI: 10.1063/1.1879112]

Atomic hydrogen has a strong technological relevance, since H atoms often serve as primary reactive particles. Typical applications can be found in areas like surface modification and thin film deposition, for example, the deposition of nanocrystalline silicon layers and diamond.<sup>1-5</sup> In this type of application, hydrogen atoms play an important role in the crystallization process and in the formation of the radicals from the precursors. Larger fluxes of H atoms allow for higher deposition rates and therefore more cost-efficient production.

Another type of application where large fluxes of atomic hydrogen can make a difference is in the area of molecule formation via plasma-activated catalysis.<sup>6</sup> In such applications the injected gases are fragmented and subsequently converted at the catalytic surface into different stable molecules. An example is the production of ammonia in  $\text{N}_2\text{-H}_2$  discharges.<sup>6,7</sup> The initial gases are partly dissociated and react on the nearby catalytic surfaces to form ammonia. Other examples are the catalytic formation of methanol and hydrazine. The production efficiency in all of these examples depends strongly on atomic fluxes.

We present measurements of the atomic hydrogen flux emerging from a cascaded arc plasma source.<sup>8</sup> The cascaded arc has the advantage of operating at high pressure, high power and small volume, leading to a high power density. The arc channel with a diameter of 4 mm and a length of 50 mm is formed by the central holes in four insulated cascade plates. A current of 60 A generates a thermal plasma in flowing hydrogen gas at a typical power of 8 kW. The molecular hydrogen flow through the arc is  $\Phi_{\text{H}_2}^0 = 1.25 \times 10^{21} \text{ s}^{-1}$  unless stated otherwise. Due to the power dissipation, a thin plasma channel is formed in the middle of the arc channel mainly consisting of atomic hydrogen. The plasma source is connected to the reactor vessel using a grounded cylindrical nozzle, which also serves as the anode. The plasma expands supersonically from the source, where the pressure is 90 mbar, into the reactor vessel, which is kept at a pressure of 1 mbar. All of the measurements presented in this letter have

been performed at axial positions close to the source.

The hydrogen atoms emerging from the plasma source are spatially probed using the two-photon absorption laser induced fluorescence (TALIF) technique.<sup>9,10</sup> A Nd:YAG laser pumped dye laser is operated at a wavelength of around 615 nm. The laser beam is frequency tripled using a KDP and a BBO crystal, resulting in tunable, 8 ns pulses at a wavelength of around 205 nm. The 205 nm photons are used to excite H atoms from the  $1s^2S$  ground state to the  $3d^2D$  and  $3s^2S$  excited states, via a two-photon transition. The resulting Balmer- $\alpha$  fluorescence is detected by a photomultiplier tube. From a spectral scan over the two-photon transition the H atom density, temperature and velocity along the laser beam are obtained. Since the laser is directed into the plasma expansion parallel to the expansion axis, axial velocities, and therefore, via the multiplication with the density, axial flux densities  $\phi_{\text{H}} = n_{\text{H}} v_z$  are determined. By moving the plasma source radially or axially, spatial profiles of the axial atomic hydrogen flux density can now be measured with a spatial resolution of less than 1 mm. In all of the measurements the dye laser wavelength is calibrated by the simultaneous recording of the well known absorption spectrum of molecular iodine. The measurements are furthermore corrected for all of the experimental parameters (laser power, optical transmission, and detector efficiency) and the linearity is checked. The densities are calibrated using a two-photon transition in a known amount of krypton.<sup>9</sup> Since the ratio of the two-photon excitation cross sections of krypton and hydrogen is known,<sup>11</sup> the relative hydrogen densities can be made absolute.

We have studied the H atom fluxes emerging from the plasma source using three different nozzles and as function of the hydrogen flow, while all other experimental parameters like arc current and background pressure are kept constant. The first nozzle has a length of  $L = 14$  mm and a constant diameter of 4 mm. This nozzle will be referred to as the long nozzle. The second nozzle has the same diameter, but its length is  $L = 7$  mm instead of 14 mm. This nozzle will be referred to as the short nozzle. In Fig. 1 the axial H atom flux density as a function of the radial position at  $z = 2$  mm from the source using the long and the short nozzle are shown.

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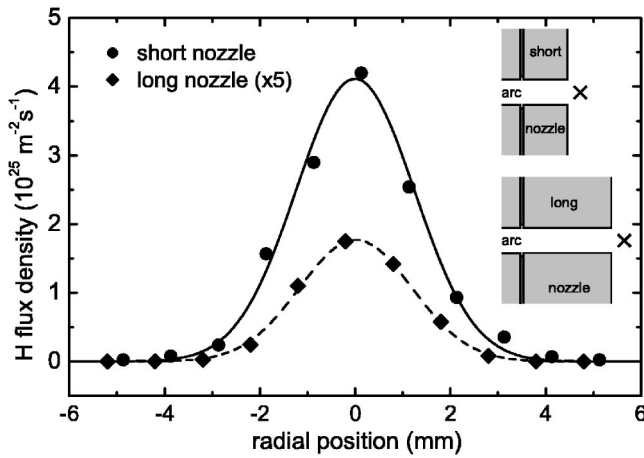


FIG. 1. Axial atomic hydrogen flux density at 2 mm from the source as function of the radial position, using the short and the long nozzle. Note that the flux densities using the long nozzle have been multiplied by 5 for a better graphical comparison. A schematic representation of both nozzles has been added. The cross indicates the measurement position.

Note that the flux density using the long nozzle is multiplied by a factor of 5 to be able to better compare it graphically. A schematic representation of both nozzles has been added to the figure. In the case of the short nozzle a maximum flux density of  $4.0 \times 10^{25} \text{ m}^{-2} \text{ s}^{-1}$  is reached on axis. From the measurements the total axial H atom flux  $\Phi_{\text{H}}$  can be determined. For the short nozzle it is  $\Phi_{\text{short}} = 4.0 \times 10^{20} \text{ s}^{-1}$  and for the long nozzle the H atom flux equals  $\Phi_{\text{long}} = 3.1 \times 10^{19} \text{ s}^{-1}$ . Using  $\Phi_{\text{H}}$ , the dissociation degree  $\beta$  can be determined via

$$\beta = \frac{\Phi_{\text{H}}}{2\Phi_{\text{H}_2}^0}. \quad (1)$$

For the short nozzle a dissociation degree of  $\beta = 0.16$  is reached at  $z = 2 \text{ mm}$ , whereas it is 0.012 using the long nozzle. This difference is rather remarkable, since the only difference is the nozzle length. In other words, the extra 7 mm length of the long nozzle induces a loss of the H atom flux of a factor of 13.

This enormous loss cannot be accounted for by volume recombination of the H atoms. At the highest density (near the wall) of  $10^{23} \text{ m}^{-3}$  and using a three-body recombination rate for H atoms of  $k^{3b} = 5 \times 10^{-44} \text{ m}^6 \text{ s}^{-1}$ ,<sup>12</sup> a characteristic time for the volume loss of H atoms of  $\tau_{3b} = 2 \text{ ms}$  can be calculated. The characteristic convection time  $\tau_{\text{conv}} = \Delta L / w_z$ , the time a particle needs to transit the extra length  $\Delta L$  of the long nozzle (7 mm) at the convection velocity  $w_z$  (around 7000 m/s), is around  $1 \mu\text{s}$ . From a comparison of these characteristic times it follows that the volume recombination is three orders of magnitude too slow to account for the loss in H atom flux.

The only other possibility, recombination of hydrogen atoms on the nozzle surface can explain the loss of hydrogen atoms, as shown by the following calculation. Since the nozzle is grounded it serves as the anode. Therefore, the current attaches to the nozzle in the first millimeter. The power dissipation into the plasma ends, and the atomic hydrogen diffuses towards the surface of the nozzle. This diffusion time varies with the radial position in the arc channel, but a good estimation is  $\tau_{\text{diff}} = 0.5 \mu\text{s}$ . This should now be compared to the characteristic time for convection  $\tau_{\text{conv}}$ . This

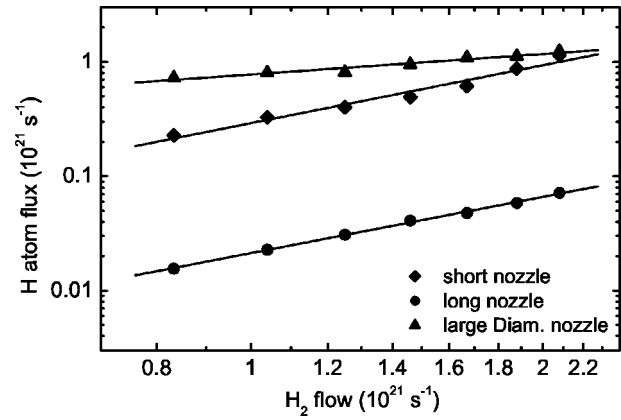


FIG. 2. Axial atomic hydrogen flux as function of the flow of  $\text{H}_2$  through the cascaded arc for three different nozzles. The flux using the short and the long nozzle has been measured at an axial position of  $z = 2 \text{ mm}$  and the flux using the large diameter nozzle at  $z = 8 \text{ mm}$ .

time also varies with the radial position via the convection velocity, but on average  $1.4 \mu\text{s}$  is a reasonable value. Assuming a recombination coefficient of  $\gamma = 0.3$  to  $-0.5$  of H atoms on copper<sup>13,14</sup> this crude estimation predicts a loss in atomic flux of around one order of magnitude over  $\Delta L$ , which agrees well with the observed factor of 13. It readily follows that, contrary to volume recombination, surface recombination does give a good explanation for the loss of atomic flux.

The atomic hydrogen flux is furthermore measured as function of the  $\text{H}_2$  flow through the arc for both the long and the short nozzle, as shown in Fig. 2. In both cases, the flux increased more than linear with increasing flow. So the dissociation degree increased with increasing flow. This reduction in the loss is explained by less efficient surface recombination. The H atom and  $\text{H}_2$  molecule densities in the arc increase linearly with the  $\text{H}_2$  flow, leading to an increase of the diffusion time of H atoms towards the surface. Therefore, the probability of an atom to reach the surface sufficiently fast decreases and with that the loss probability via surface recombination. Hence more atoms survive the transit through the nozzle.

Several improvements can now be implemented using the knowledge that surface recombination is the main loss channel for hydrogen atoms. First, the wall should be as far from the plasma as possible and second, also in the nozzle region power should be dissipated, to better confine the plasma. Both these improvements are accomplished using a nozzle with a larger diameter. Using this nozzle, there is a sudden increase in the radius from 2 mm to 6 mm after the last cascade plate, enlarging the distance between surface and plasma. Furthermore, the current cannot attach immediately at the beginning of the nozzle, but attaches further down on the nozzle, dissipating power further downstream compared to the situations using the short and long nozzle. A schematic representation of the nozzle is given in Fig. 3.

The results for the atomic hydrogen flux are shown in Fig. 3, where the radial profile of the flux density at  $z = 8 \text{ mm}$  in the large diameter case is compared to that of the short nozzle at 8 mm. Note that the distance  $z$  is the distance from the last narrow opening, as indicated in the figure. Equal  $z$  now means equally far expanded. Since in the case of the large diameter nozzle no velocities could be determined because of a too low signal-to-noise ratio, the velocities using the short nozzle at the corresponding position have

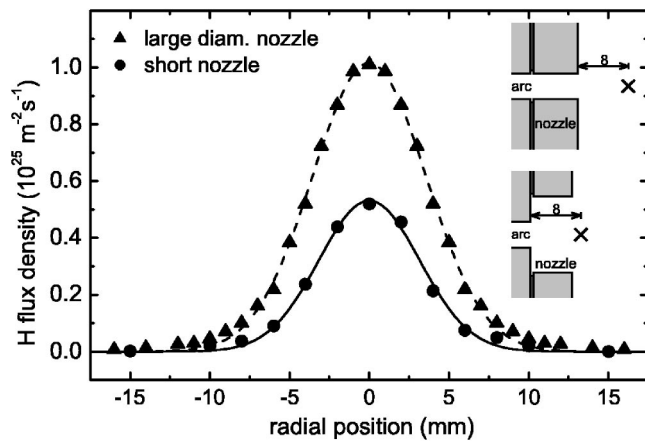


FIG. 3. Axial atomic hydrogen flux density at 8 mm from the source as function of the radial position, using the short nozzle and the large diameter nozzle. A schematic representation of both nozzles has been added. The cross indicates the measurement position.

been used. This procedure is supported by the fact that a freely expanding plasma cannot reach any surface of the nozzle/source in the large diameter case, so the expansion is in terms of velocity identical to the expansion using the short nozzle. The induced error is estimated to be within 25%. The atomic flux at  $z=8$  mm using the large diameter nozzle is  $\Phi_{\text{largeD}}=8.1 \times 10^{20} \text{ s}^{-1}$ , whereas it is  $\Phi_{\text{short}}=3.3 \times 10^{20} \text{ s}^{-1}$  using the short nozzle. So due to the change in geometry, the dissociation degree has increased to a value of  $\beta=0.33$  at  $z=8$  mm in the expansion. This corresponds to equal fluxes of molecular and atomic hydrogen.

The H atom flux using the large diameter nozzle may even be higher than observed at 8 mm. Compare for example the decrease in atomic flux using the short nozzle when moving downstream. It decreases by 17% when moving from  $z=2$  mm to 8 mm. This effect has been extensively studied, both in a pure  $\text{H}_2$  expansion and in  $\text{Ar-H}_2$  expansions<sup>10,15</sup> and is explained by the diffusion of H atoms out of the expansion. This diffusion is induced by H atom density gradients between the background gas in the vessel and the plasma. The H atom background density is low due to surface recombination of the hydrogen atoms on the vessel walls. Assuming the loss of H due to diffusion in the large diameter nozzle case is the same as for the short nozzle case, a total flux at 2 mm in the large diameter case of  $9.8 \times 10^{20} \text{ s}^{-1}$  can be calculated, which indicates a dissociation degree of 0.4.

The flow dependence of the H atom flux using the large diameter nozzle is much less strong than with the other nozzles. It showed a slightly less than linear increase with the  $\text{H}_2$  flow, for a slightly decreasing dissociation degree, see Fig. 2. This would point to near total dissociation of the plasma emerging from the plasma source. The fact that the measurements at  $z=8$  mm point to a dissociation degree of 0.33 rather than a value close to 1 can partly be explained by the estimated error in the measurements of 20–30%. However, another, more probable, explanation is that the H atoms diffuse out of the expansion during the first few millimeters, where the wall, and thus the loss channel for H atoms, is not too far from the plasma.

We conclude that the nozzle has a determining influence on the flux of atomic hydrogen emerging from the plasma source. The main loss channel for the atomic hydrogen is surface recombination on the nozzle surface. By implementing some relatively small changes in the nozzle shape, the dissociation has already increased from around 1% to more than 33% and H atom fluxes of more than  $10^{21} \text{ s}^{-1}$  are reached. Besides an effect on the radical flux, surface processes are also believed to influence the ionic fluxes, which is confirmed by the variation in plasma emission of several orders of magnitude between the different nozzles.

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