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Plasma expansion: fundamentals and applications

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Abstract

The study of plasma expansion is interesting from a fundamental point of view as well as from a more applied point of view. We here give a short overview of the way properties like density, velocity and temperature behave in an expanding thermal plasma. Experimental data show that the basic phenomena of plasma expansion are to some extent similar to those of the expansion of a hot neutral gas. From the application point of view, we present first results on the use of an expanding thermal plasma in the plasma-activated catalysis of ammonia, from N_2–H_2 mixtures.

1. Introduction

Expanding plasmas are widely used in processes like etching, deposition, nitriding, waste treatment and treatment of archaeological artefacts. In all these processes the efficiency with which a specific particle, i.e. an ion, electron or atomic or molecular radical, can be produced is one of the most important issues that has to be addressed. The consequence is that the physics of plasma expansion has to be studied on a fundamental basis [1]. Flow dynamics, density, temperature and velocity behaviour in the plasma jet [2–4] have to be known in order to be able to optimize the efficiency of the source. Numerical simulations can be used to optimize and to help understanding the plasma processes taking place in the expansion and possibly also in the plasma surface interaction region [5]. Models can also give generic information on the physics of expanding plasma, such as on shock formation, recombination, excitation, wall association and re-circulation [6–8].

The need to get a better understanding of the processes taking place in the thermal plasma expansion at the Eindhoven University has led to the introduction of numerous laser diagnostic techniques such as: Thomson–Rayleigh scattering [9], coherent anti-Stokes Raman scattering [10], (two-photon) laser induced fluorescence [11–14] and cavity ring down spectroscopy [15, 16]. These studies provide almost complete sets of data of our expanding thermal plasma in terms of density, temperature and velocity of electrons, ions, atomic and molecular radicals.

We here give a short introduction into the description of plasma expansion, which, as we have shown, does very often not differ much from a hot gas expansion. With two examples we show the importance of the more fundamental oriented studies for the optimization of applications of our thermal plasma expansion. These examples are the deposition of amorphous hydrogenated carbon and silicon [17, 18] and the small scale generation of ammonia.

2. Fundamentals of plasma expansion

The basic phenomena of plasma expansion are to some extent similar to those of the expansion of a hot neutral gas, and can thus be described using the supersonic free jet theory. A schematic view of an expansion with its characteristic features is shown in figure 1.

2.1. Density development

The density development along the jet centreline, for example, can be determined using the conservation law and assuming that particles originate from a virtual point source and flow along straight stream lines:

$$n(z) = \frac{n_0}{1 + (z/z_0)^2}. \quad (1)$$

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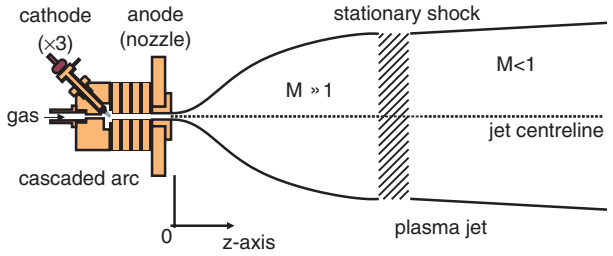

Figure 1. A cascaded arc plasma source and a schematic view of an expansion with its characteristic features.

Here n_0 equals the density at the source exit ($z = 0$). In equation (1) z_0 is a scaling length, introduced to allow for a comparison of measurements with nozzles with different diameters ($z_0/d \approx 0.5$). At the start of the expansion, i.e. where the axial location is less than a few nozzle diameters, this expression differs slightly from the one used in gas dynamics [19]. This modification is connected with the plasma character of the source region with its high temperature, sonic exit velocity and finite temperature gradients. It allows for a zero first derivative of the density at the source point in order to accommodate for the convective processes in the source, as well as for field generation. Close to the nozzle the density decreases in the radial direction from the centre of the jet to the outside. However, further away from the nozzle this hill-like structure gradually weakens and can eventually go over in a valley-like structure. At this position in the plasma, the density on-axis is lower than the density in the background—the so-called overexpanded region. At the end of the supersonic expansion a stationary normal shock is formed, which is the front boundary of the barrel shock structure. Both the position and the thickness of the stationary shock depend on the background pressure. Throughout the stationary shock front, of which the thickness is of the order of one local momentum exchange mean free path, the velocity decreases, and the temperature rises, due to collisions with the background gas. Therefore, due to conservation of forward flux, the density increases abruptly. The Rankine–Hugoniot relations connect such a jump to the Mach number magnitude ahead of the shock wave. Behind the shock wave, the plasma expands subsonically into the background. It has been shown experimentally and also observed in simulations that to a good approximation the beam width stays constant in the subsonic part [14, 20].

2.2. Temperature development

If the supersonic part of the expansion is assumed to be adiabatic, the energy equation reduces to Poisson's adiabatic law:

$$\frac{T(z)}{T_0} = \left(\frac{n(z)}{n_0}\right)^{\gamma-1}, \tag{2}$$

where T_0 denotes the temperature at the source exit and γ is the effective value for the specific heat ratio, i.e. $\frac{5}{3}$ for an isentropic flow of a monoatomic gas. In neutral gas expansion the flow is isentropic in the supersonic domain and the temperature profile can be well described by equation (2). For a thermal plasma, the effect of charged particles on the specific heat ratio has been calculated by Burm *et al* [21]. They concluded that $\gamma \approx 1.2$ for a wide range of the ionization degree (0.03–0.3). In plasma expansion of a monoatomic gas, the temperature decrease is found to be less than predicted by equation (2), but can be well described assuming a smaller value for γ. Heat conduction of heavy particles and recombination of charged particles keep the temperature higher than in a neutral gas expansion. For example, in the case of an argon/hydrogen plasma expansion, the specific heat ratio is found to be about 1.4 for the hydrogen and argon atoms [11, 12].

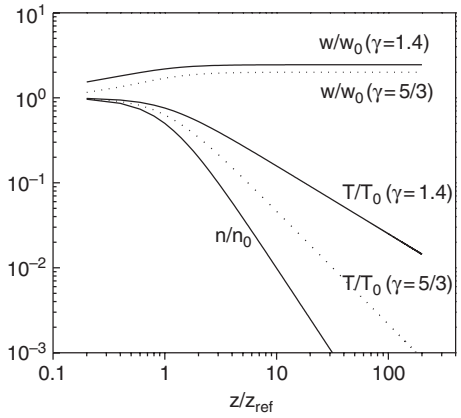

Figure 2. Calculated density, temperature and velocity behaviour of particles in the supersonic part of an expanding plasma jet, for two different adiabatic constants.

2.3. Velocity development

From a simplified momentum balance (no viscosity, no Lorentz forces) and assuming a quasi-adiabatic expansion, the following relation for the velocity w_z on the jet axis can be deduced [19]:

$$w_z = c_{s_0}\left[1 + \frac{2}{\gamma - 1}\left(1 - \left(\frac{1}{1 + (z/z_0)^2}\right)^{\gamma-1}\right)\right]^{1/2}. \tag{3}$$

Here c_{s_0} denotes the sound velocity at the nozzle exit ($z = 0$). We assume that the Mach number, $M = w_z/c_s$, at the nozzle exit equals 1. From equation (3) it can be shown that the velocity of the expanding gas cannot exceed $w_{\max}$ [19]:

$$w_{\max} = c_{s_0}\sqrt{\frac{\gamma + 1}{\gamma - 1}}, \tag{4}$$

and that $w_{\max}$ is reached after a few diameters of the exit nozzle. This means that the mass and the heat capacity of the expanding gas mixture and the temperature at the nozzle exit, T_0, determine the maximum velocity to which the gas mixture can be accelerated.

It has been experimentally established for the supersonic domain of plasma expansions that the density rarefaction, the velocity as well as the temperature follow the common gas expansion laws, with a smaller adiabatic exponent, at least for neutrals and charged particles [14, 22]. In figure 2, the theoretical behaviour of expansion quantities is depicted as a function of the axial position (relative to the scaling length z_0) for isentropic as well as non-isentropic conditions. In the case of radicals, however, the density rarefaction differs strongly from the classical picture [11].

2.4. The hydrogen and nitrogen plasma expansion

Plasma jets containing hydrogen or nitrogen have been studied by means of two-photon absorption laser induced fluorescence (TALIF) [23]. This technique allows for the spatially resolved determination of density, temperature and velocity of, for example, ground state hydrogen and nitrogen atoms. In figure 3 the density behaviour of ground state hydrogen and nitrogen atoms, in an expansion produced from a thermal hydrogen and nitrogen plasma, is shown. Surprisingly, in the case of hydrogen no density jump is observed across the shock front, while the velocity is measured to decrease and the temperature development on-axis clearly shows the shock structure (see figure 4) [11]. The loss of hydrogen atoms in the supersonic part of the expansion cannot be explained by volume association of hydrogen atoms to form hydrogen molecules, since this reaction is much too slow under the experimental conditions in the jet. The anomalous H atom density profile arises from the partial pressure induced diffusion of hydrogen atoms, which exists because of the very efficient association of hydrogen atoms at the vessel wall. Due to this association, the wall of the vessel acts as a sink for hydrogen atoms, thus inducing a very high density gradient between the core of the supersonic jet and the surrounding background gas.

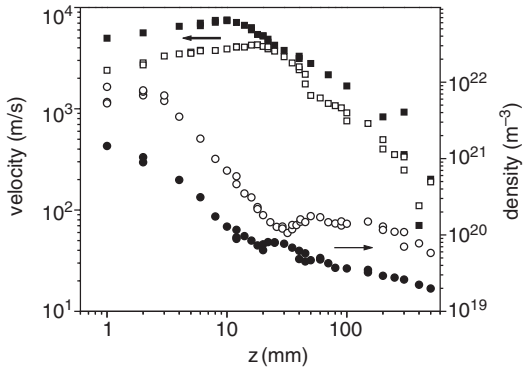

Figure 3. Measured ground state hydrogen (●, ■) and nitrogen (○, □) atom density (circles) and velocity (squares) in an expansion produced from a thermal hydrogen and nitrogen plasma. The background pressure was 20 Pa.

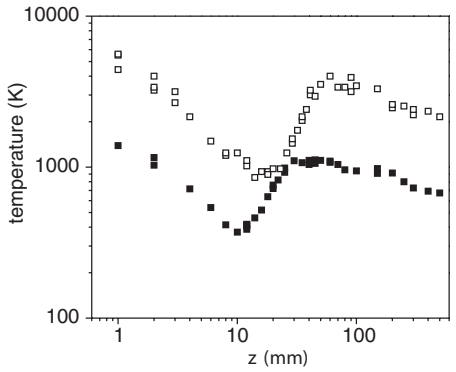

Figure 4. Measured ground state hydrogen atom (■) and nitrogen atom (□) temperature in an expansion produced from a thermal hydrogen and nitrogen plasma. The background pressure was 20 Pa.

In the case of nitrogen, a small jump is observed in the density around 30 mm. However, the density increase is less, by more than a factor of 2, than expected from the velocity measurement and the Rankine–Hugoniot relations. Here the association at the vessel wall is less efficient and due to the heavier mass as compared to hydrogen, the diffusion is less, i.e. the nitrogen atoms will be better confined in the supersonic part of the plasma expansion (see figure 3).

3. Application of plasma expansion

Plasma expansion has been successfully used for, for example, surface treatment, deposition and etching. One of the advantages of a supersonic expanding thermal plasma jet is the fact that plasma production, plasma transport and the treatment area are geometrically separated, i.e. the so-called remote plasma approach (see figure 5). Also, due to the supersonic part of the expansion, the conditions in the downstream plasma zone do not influence the plasma source. The plasma source, in our case a cascaded arc, is used to produce the active species, i.e. electrons, ions or atomic radicals. In the supersonic expansion, however, the electron temperature decreases so much that dissociation by electrons is not possible and the gases used for deposition or etching and injected close to the stationary shock, are dissociated by ions or (atomic) radicals. In the subsonic part of the jet they are subsequently transported to the treatment area. Due to the geometrical separation of source and treatment area, the substrate or the surface to be treated can be independently controlled from the plasma source in terms of temperature or electrical potential.

We here show two examples in which the expanding thermal plasma technique is used, i.e. in the fast deposition of thin layers and in the plasma-activated catalytic production of ammonia.

3.1. Deposition

In the fast deposition of thin layers, large fluxes of radicals are needed. For the production of these radicals both ions

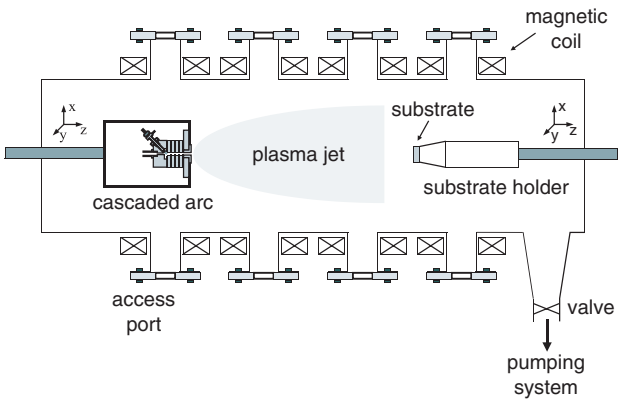

Figure 5. Setup for expanding thermal plasma jet in which both plasma surface interaction and deposition can be studied. Typically the arc is operated at sub-atmospheric pressure (0.5 atm). A current of 50 A is used to create a 1 eV thermal plasma. The plasma expands from a nozzle into a vessel at low pressure (20–100 Pa). Both the plasma source and the substrate holder can be moved in the x, y and z direction.

and primary radicals (produced in the source) can be used. In the case of fast production of amorphous hydrogenated carbon (a-C : H), it has been established that the ion route starting from acetylene gives the best result in terms of hardness and deposition speed [17]. The C_2H radical is the most important specie in the formation of a-C : H layers. This radical is formed via charge exchange and dissociative recombination of acetylene:

$$C_2H_2 + Ar^+ \rightarrow C_2H_2^+ + Ar, \quad (5)$$

$$C_2H_2^+ + e^- \rightarrow C_2H + H. \quad (6)$$

In this way deposition speeds up to 100 nm s^{-1} are achieved. In the case methane is used, the deposition speed is much lower. Here, CH_2 and CH_3 are formed, radicals that have a much lower sticking probability than C_2H. Due to the long residence time of these radicals in the plasma reactor, they can associate and form, for example, larger hydrocarbons like acetylene.

In the case of amorphous hydrogenated silicon (a-Si : H), the radical route has shown to give the best results in terms of electrical properties and index of refraction [18]. The ion route leads to the formation of SiH_2 and SiH, radicals that have a very high sticking probability, which leads to very rough surfaces and layer properties which are not suitable for solar cells. The radical route leads to SiH_3 via the abstraction reaction:

$$H + SiH_4 \rightarrow SiH_3 + H_2. \quad (7)$$

In this way deposition speeds in the order of 10 nm s^{-1} can be reached and the layers that are formed have the right properties to be used for solar cells.

3.2. Plasma-activated catalysis

If a surface is exposed to fluxes of radicals, the radicals adsorb at the surface. If the fluxes are so high that within the residence time several mono-layers can cover the surface, some radicals will be in a physisorbed state. At low pressure the density of radicals at the surface becomes much higher than the density in the gas phase, and the recombinative desorption of radicals increases drastically. In this desorption reaction excited (stable) molecules can be formed that can recirculate in the vessel. This means that starting from an atomic radical plasma source, due to plasma surface interaction, molecules are formed that can influence the dynamics of the plasma flow. An example of this is the formation of ro-vibrationally excited hydrogen molecules at a surface that is exposed to a hydrogen plasma. Depending on the state in which the hydrogen atom is attached to the surface, the hydrogen molecule can be formed in the electronic ground state, but highly vibrationally excited to about $v = 10$ if the hydrogen atom is physisorbed, or $v = 5$ if it is chemisorbed [24]. In the case of nitrogen it becomes slightly more complicated due to the manifold of electronic states in which the nitrogen molecules can be formed. Most of these states are triplets, and thus not radiatively coupled to the electronic ground state, but to the first electronically excited state ($N_2(A)$). In the case of low pressure, density can build up in this chemically active state. Plasma takes care of the dissociation, while surface coverage of atoms or radicals enhances the chemical activity: plasma-activated catalysis.

A system that is being studied is the formation of ammonia in plasma created from nitrogen–hydrogen mixtures. At low pressures, ammonia is mainly produced at the vessel wall via stepwise production. Starting from N and H, via NH and NH_2, NH_3 is formed [25–27]. In studies in which the surface, e.g. Pt or Rh, is used to enhance the dissociation of the precursor molecules, it has been established that the dissociation probability of the precursor molecules decreases when the surface coverage is very high, i.e. there are not enough vacant surface sites available [28]. In plasma-activated catalysis the plasma source delivers the atomic radicals and the adsorbed hydrogen atoms accelerate the formation of ammonia. Questions that have to be answered are the selectivity of the production process, for example, can one selectively produce NH_3 or N_2H_4 by tuning the experimental parameters, like surface material or temperature, or the relative fluxes of nitrogen and hydrogen atoms.

We used cavity enhanced absorption spectroscopy to determine the absolute density of ammonia [29]. In figure 6 part of the recorded vibrational overtone spectrum is shown. The experimental conditions were: $I_{arc} = 55$ A, the flow through the arc consisted of 0.56 slm N_2 and 1.42 slm H_2 and the background pressure was 20 Pa. Preliminary results show that when both gases were introduced in the cascaded arc, ammonia is produced most efficiently; at $P_{bg} = 20$ Pa about 0.2 Pa is ammonia. Experiments with an expanding thermal hydrogen plasma to which nitrogen is added in the background showed no measurable amount of ammonia. In the opposite situation, i.e. pure nitrogen plasma and hydrogen added in the background, the production can be of the order of a few tenths of a per cent of the background pressure. The reason could be that in the case of a nitrogen plasma, the nitrogen ions in the expanding thermal plasma jet can dissociate the hydrogen molecules in the background, but if one starts from a hydrogen plasma, the hydrogen ions cannot dissociate the nitrogen molecules [30]. Also the nitrogen ion flux leaving the arc in a pure N_2 plasma is higher than the hydrogen ion flux leaving the arc in a pure H_2 plasma. Other systems that can be studied are, for example, the formation of methanol from oxygen and methane. In this way the methane, which

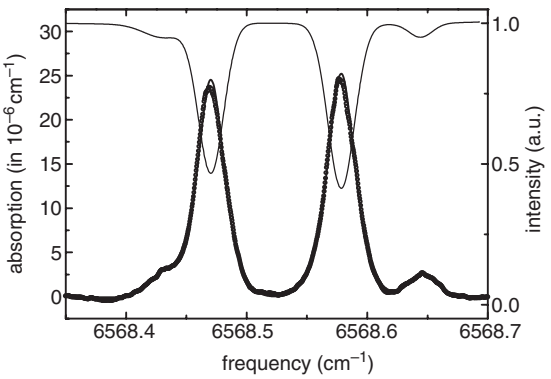

Figure 6. The lower curve (○) shows part of the NH_3 spectrum measured in the subsonic region of an expanding thermal plasma. The plasma is created in a cascaded arc from a mixture of H_2 and N_2 (flow ratio 2.5 to 1). The total background pressure is 20 Pa. The solid line shows a fit with 4 Gaussians through the measured spectrum. The upper curve shows the single pass absorption spectrum of ammonia in a reference cell.

is now very often a 'burned-without-use' by product of, for example, oil refining industry, can be transported more easily and used somewhere else [31–33].

4. Conclusions

We have presented an overview of the work performed at the Eindhoven University on plasma expansion. One of the results shows that the expansion of an argon plasma from a high-pressure source into a low-pressure vessel resembles that of a hot neutral gas expansion with a minor modification in the adiabatic exponent. However, when hydrogen or nitrogen is added to the argon gas, or when pure hydrogen or nitrogen gas is used, the behaviour of the atomic hydrogen and nitrogen radicals in the expansion differs strongly from the classical behaviour, mainly because of the influence of the presence of surfaces.

The understanding of the fundamentals of plasma expansion allows for the extent of applications of this phenomenon. For quite some time, this technique is used for deposition, etching, nitriding and treatment of surfaces. We have shown the first preliminary results on the use of plasma expansion in the generation of ammonia via plasma-activated catalysis.

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