Wall Association and Recirculation in Expanding Thermal Arc Plasmas

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In recent years, extremely rapid recombination as well as other effects in expanding thermal arc plasmas have been attributed to wall association of radicals (mainly H) and recirculation in the expansion vessel. Coherent anti-Stokes Raman scattering measurements on H_2 and HD when the arc burns on a mixture of H_2 and D_2 show new evidence for this view.

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Models and experiments in the field of plasma chemistry generally focus on the description of radical kinetics and radical detection. Because of the very complex plasma kinetics (literally hundreds of reactions may be involved), global understanding is difficult to attain [1]. In this Letter we want to specifically address the formation of stable molecules, which appears to dominate the plasma we have studied and may play an essential role in many other types of plasmas as well. The simple view resulting from this consideration may rapidly lead to a clear understanding of the plasma chemistry in many cases.

Plasma deposition and etching techniques are becoming ever more important tools for the manufacturing of small structures in semiconductor materials, as well as for the coating of materials with thin films (e.g., amorphous hydrogenated carbon and silicon, diamond, graphite) [2]. Plasma sources are also used for the creation of useful particles, such as H^- ions, H^+ ions, or H radicals (e.g., [3,4]). Different types of plasma generators are used (rf, microwave, dc) for the creation of deposition precursors or (etching) radicals, but a common factor is a fairly large (5–100 liters) vacuum vessel, usually made out of stainless steel. The question now is to what extent the composition of the source plasma is representative for the composition in the vacuum treatment vessel. The *residence time* of a particle in the vessel can attain appreciable values, seconds or more. This implies the principal possibility of many wall reactions, with a pronounced influence on the radical (and stable molecule) populations in the treatment region. The important case of wall association of H radicals into H_2 molecules, for example, has received considerable attention in the literature (e.g., [5]).

In this study, a dc wall stabilized thermal arc plasma source is used for the deposition of thin films [6] and as a hydrogen particle source [4]. The thermal, subatmospheric plasma is allowed to expand into a low-pressure vessel (volume around 100 liters), creating an expanding plasma jet (see Fig. 1). Monomers (C_2, H_2, CH_4, SiH_4) can be injected in the jet (i.e., downstream) and deposition takes place on a downstream substrate. The arc is usually operated in pure argon or in a mixture of argon and hydrogen. In the case of a particle source the carrier gas is pure hydrogen. In all these cases residence times are around 0.3–2 sec, and a recirculation flow is present in the vessel. These characteristics favor a major role for wall processes, leading to the formation of stable molecules from radicals (e.g., H_2 from H and H). The plasma is recombining and afterglowlike, with low electron temperatures (T_e around 0.2 eV) and low electron densities [n_e around 10^{16} m^{-3}, when H_2 is used in considerable amounts (e.g., 10 vol % H_2 in argon [4])]. These T_e and n_e values rule out a major importance for electron kinetics.

The research on the above mentioned wall phenomena is performed with the experiment in Fig. 1 [7]. As the wall association process creates a population of stable molecules around the plasma jet itself, i.e., in the "dark" periphery, active (laser) plasma diagnostics have to be employed in order to obtain the required data. As this study focuses on argon-hydrogen and pure hydrogen plasmas, a high-sensitivity coherent anti-Stokes Raman scattering (CARS) spectroscopy experiment has been realized to perform density and temperature measurements on rovibrationally excited H_2 (and HD, when the arc operates on a H_2/D_2 mixture). The aim is to prove that the measured amounts of stable molecules around (and in) the plasma can only be explained by assuming that wall association and recirculation are dominant processes.

The CARS spectrometer is a scanning boxcars experiment, using a reference branch in order to cancel out experimental peculiarities, such as a specific dye response

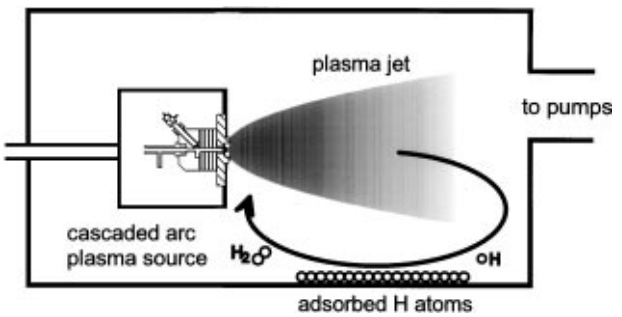

FIG. 1. A schematic of the experimental arrangement showing the thermal plasma source and the stainless steel vacuum vessel. The envisaged recirculation pattern (see main text) has been sketched, as has the wall association of H radicals into H_2 molecules (in the case of H_2-containing plasmas).

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spectrum. The experiment will be described in detail in a forthcoming paper [8]; CARS specifics can be found in review articles (e.g., [9]). At this moment it suffices to note that the setup is very sensitive, capable of state-selective detection of H_2 at very low pressures (a spectrum can be taken at 0.1 Pa H_2 at 300 K). A 3 : 1 mixture of Exciton DCM and Exciton LDS698 dyes has been used to cover the H_2 and HD spectral regions, in a Raman shift range of 4165–3000 cm^{-1}. Absolute total density calibration to an accuracy of $\pm 10\%$ is possible. Using the appropriate correction factors for the Raman cross sections [10], absolute HD state densities can also be determined. Effects of saturation in the CARS spectrum [11] have been shown to be negligible for our laser powers [8]. Spatial resolution is obtained by crossing the beams (boxcars): The detection volume has a length of ≈ 2 cm and a diameter of ≈ 180 μm.

It is useful to take a look at the general characteristics of the argon-hydrogen plasma by considering some Thomson scattering results presented in Fig. 2. The n_e values have been measured on the axis of the expanding jet and show the behavior of an argon plasma with small amounts of hydrogen added. A very pronounced influence is observed, even for very low hydrogen seed fractions. The hydrogen is admixed to the argon flow before it enters the arc. The plasma conditions are the following: arc current $I_{\text{arc}} = 45$ A, voltage $V_{\text{arc}} = 50$ V, total flow 3.5 standard liters per minute (SLM), and vessel background pressure $p_{\text{back}} = 40$ Pa. The hydrogen admixtures are percent by volume. The anomalously fast recombination has been attributed to the formation of ArH^+ molecular ions from Ar^+ and H_2. This strongly points to wall association, as H_2 molecules are very unlikely to survive the 1 eV environment of the plasma inside the arc, especially at lower seed fractions. In this view, only Ar^+, H^+, Ar, H, and e^- leave the arc, forcing the wall to be considered as the major source for H_2 molecules needed to explain the fast recombination [12].

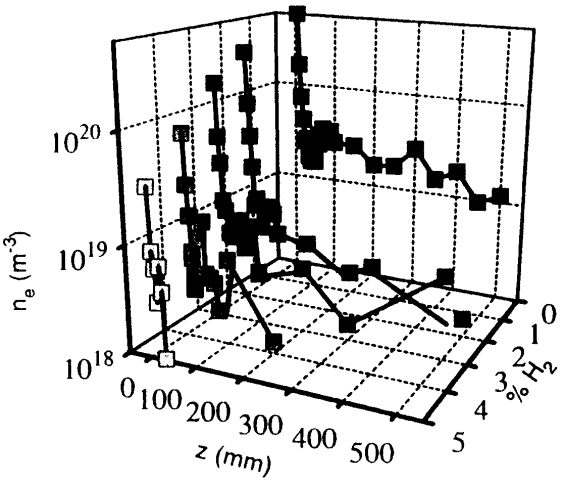

FIG. 2. Thomson scattering data for the electron density versus axial position for pure argon and different hydrogen-argon admixtures. The axial position z increases with increasing downstream distance from the nozzle. The impact of small additions of H_2 to the flow is clearly visible.

The measurements that have been performed are the following: (1) CARS measurements on 10 vol% H_2 in argon mixtures. Hydrogen is added to the flow before it enters the arc (arc injection), but in a second experiment it is flushed directly into the vessel, the arc operating on pure argon (vessel injection). (2) CARS measurements on H_2 and HD when the arc burns on a 50/50 mixture of H_2 and D_2. (3) Ditto with the arc burning on H_2, while D_2 is flushed into the vessel. (4) Ditto with the arc burning on D_2, with H_2 flushed into the vessel.

CARS on Ar-H_2 mixtures.—In order to prove the existence of similar populations of H_2 around the plasma for arc and vessel injection, CARS measurements are carried out under the following conditions: $I_{\text{arc}} = 45$ A, flow = 3.5 SLM, $p_{\text{back}} = 140$ Pa, 10 vol% H_2 in Ar. The results for the H_2 partial pressures (taken as the product of total density of all measured states, the rotational temperature, and the Boltzmann constant) are depicted in Fig. 3. The radial scan is made by moving the plasma inside the vessel, as this can be done without significantly changing the plasma [7]. The plots clearly show that in both cases (vessel and arc injection) the partial pressure of H_2 in the periphery of the jet equals 10% of p_{back}, within the measurement accuracy. As we have to assume an almost complete dissociation of H_2 in the arc at these seed fractions, this means that the measured H_2 in the arc injection case must have been formed at the vessel walls, as it can be shown that volume association of H radicals to H_2 through three-body processes cannot be of significant influence in our case [13].

CARS on H_2-D_2 mixtures.—In this case the conditions are the following: $I_{\text{arc}} = 37.5$ A, $V_{\text{arc}} = 100$ V, flow = 3.5 SLM (50% H_2 and 50% D_2 by volume, both injected in the arc), and $p_{\text{back}} = 40$ Pa. Measurements on H_2 and HD concentrations and temperatures are performed both in the plasma [at axial position $z = 70$ mm (z denotes the distance from the onset of the expansion) and a radial position $r = 0$] and in the periphery (at $z = 20$, $r = 20$ mm). In the latter case the laser beams are clearly *over* the plasma jet. For the axis of the jet, at an axial position of $z = 70$ mm, rotational Boltzmann plots for both H_2 and HD are given in Fig. 4. A summary of the results is given in Table I, clearly pointing to a total mixing in the formation of products as $H_2 : HD : \text{rest} = 1 : 2 : 1$ in partial pressures (and densities as well as the temperatures are very similar). We think it safe to assume that the "rest" will consist mainly of D_2. At this moment, D_2 is outside the measurement range, as it would require different experimental conditions (dyes, dichroics).

A discussion of these measurements necessarily starts with an evaluation of the dissociation degree inside the cascaded arc. This dissociation degree has been measured by power input measurements on pure H_2 arcs and has been determined to be around 70% (of the input flow) for an arc current of 37.5 A [14]. The fact that we

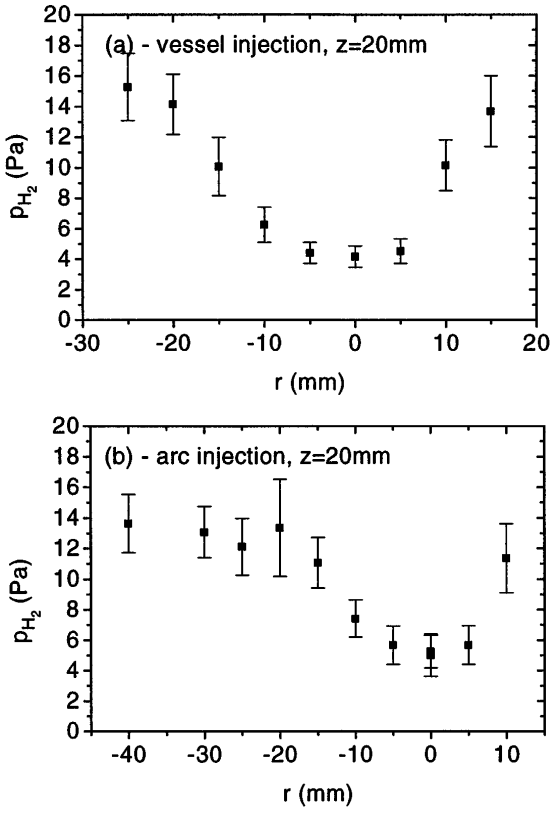

FIG. 3. Radial profiles at a downstream distance of 20 mm for the H_2 partial pressure in a 10 vol% H_2 in Ar mixture. Graphs are shown for both vessel (a) and arc (b) injection. The background pressure is 140 Pa.

observe (also in pure hydrogen [8,15]) a *low* dissociation degree inside the vessel (maximum 10%), a vessel (i.e., wall) association process must be considered. Assuming that, in the above case, 70% of the particles leaving the arc are H and D radicals, the walls must be saturated with H and D; subsequent association and desorption of molecules should lead to the observed $H_2:HD:D_2$ ratio of 1 : 2 : 1. The 30 vol% of molecules leaving the arc are most probably of the same constitution, as perfect mixing is to be expected there. The final mixture in the vessel corresponds exactly with the measurement results.

A point of concern are volume reactions of the type

$$H + D_2 \rightarrow HD + D, \quad (1)$$

$$D + H_2 \rightarrow HD + H. \quad (2)$$

These reactions have been studied extensively [16] and show a significant threshold behavior at low temperatures. At temperatures inside the vessel (400–1200 K [8] and Table I), these reactions can be neglected in a first approximation (at rates around 10^{-21}–10^{-18} m^3s^{-1}) as can the analog reactions with *ions* instead of radicals [17], in view of the low ion densities. In the arc, however, at high densities and temperatures, these reactions can play a dominant role [higher ion densities, higher rates for (1) and (2)] leading to total mixing there (but *not* to a lower dissociation degree).

H_2 and HD CARS on other H_2-D_2 mixtures.—In this last set of measurements, the arc is operated on either full H_2 or D_2 (37.5 A, 2 SLM), while the other constituent is flushed directly in the vessel (1 SLM, $p_{back} = 40$ Pa). So here we encounter the situation where only H (D) radicals leave the arc (representing a 70% dissociation degree in the arc), whereas D_2 (H_2) is injected in molecular form. Table II shows the remarkable results: The HD density is very low (partial pressure 1.2 Pa) in the case of a D_2 arc, and the HD signal even drops to the detection limit in the case of a H_2 arc. Following the reasoning above, this means that there is no full dissociation of the vessel-injected molecules. No total mixing can thus occur at the vessel walls. Some conversion to HD is observed, however, and so some dissociation must occur in the volume. This leads to the conclusion that reactions (1) and (2) are responsible for dissociation of a small part of the vessel-injected molecules. Note that dissociation processes through these volume reactions leads to HD production as well. Volume processes can also play a minor role when H_2 and D_2 are injected in the arc, but evidently they cannot account for total mixing: This can only be the case when most of the molecules are dissociated (in

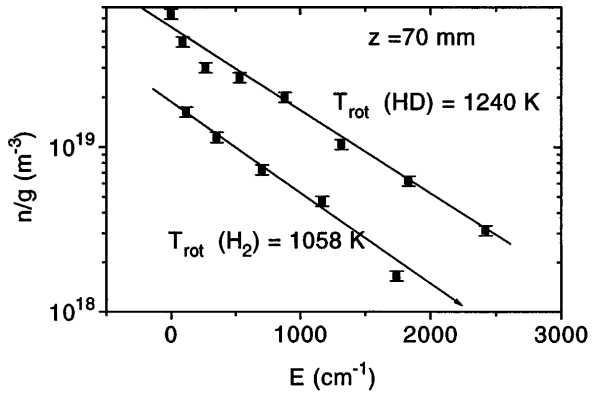

FIG. 4. An example of Boltzmann plots constructed from the H_2 and HD measurements in the plasma (i.e., at $z = 70$ mm and $r = 0$).

TABLE I. The CARS results for HD and H_2. Experimental errors are around 7%–10% for T_{rot} and n. The resultant error for the pressure should be around 14%–20%. The experimental conditions are $p_{back} = 40$ Pa, $I_{arc} = 37.5$ A. Flows: H_2-D_2 arc: 1.75 SLM H_2 and 1.75 SLM D_2.

		H_2-D_2 arc Periphery ($z = 20$ mm) ($r = 20$ mm)	H_2-D_2 arc Plasma ($z = 70$ mm) ($r = 0$ mm)
HD	T_{rot} (K)	398	1240
HD	n (m^{-3})	4.1×10^{21}	9.5×10^{20}
HD	nkT (Pa)	22.2	16.3
H_2	T_{rot} (K)	383	1058
H_2	n (m^{-3})	2.1×10^{21}	5.1×10^{20}
H_2	nkT (Pa)	10.9	7.5

TABLE II. The results of the HD and H_2 CARS measurements. The arc is burning on either H_2 or D_2, the other constituent (D_2 or H_2, respectively) is flushed into the vessel. Conditions are $p_{back} = 40$ Pa, $I_{arc} = 37.5$ A. Flows: H_2 arc: 2 SLM H_2 in arc, 1 SLM D_2 in vessel; D_2 arc: 2 SLM D_2 in arc, 1 SLM H_2 in vessel.

		H_2 arc Periphery ($z = r = 20$ mm)	D_2 arc Periphery ($z = r = 20$ mm)
HD	T_{rot} (K)	≈375	375
HD	n (m^{-3})	$\approx 3 \times 10^{19}$	2.4×10^{20}
HD	nkT (Pa)	≈0.15	1.2
H_2	T_{rot} (K)	373	343
H_2	n (m^{-3})	4.0×10^{21}	3.1×10^{21}
H_2	nkT (Pa)	20.7	14.5

the arc) when they enter the vessel. The rates given in Ref. [16] confirm the marginal importance of volume reactions.

The asymmetry between the H_2 and D_2 arc cases is very interesting and may be attributed to three effects: (a) the arc is slightly more efficient when operated on D_2 (more D radicals); (b) at lower temperatures, the rate for reaction (1) can be as many as 8 times slower than that for reaction (2) (Ref. [16]); (c) wall adsorption may be more efficient for H than for D radicals.

The above measurements can be used to formulate a rough model of the expanding arc plasma with a dominant role for recirculation. We start by looking at the residence time in the 300 liter vessel, which is around 2 s for the given flows and pressures (40 Pa, 3.5 SLM). The transit time of a particle through the beam (at an estimated speed of 3000 m/s) is around 0.3 ms and a comparison of the volumes of the beam and the periphery leads to an estimated recirculation time of 25 ms. From these values, the number of recirculations per residence time follows to be 80, so each paricle can "see" the wall very often. This would lead to a complete association at the wall even at values for the association coefficient (the probability of a H_2 molecule leaving after a collision of H with the H-saturated wall) as low as 0.05. In this picture, the radicals leaving the arc are completely recycled in the form of stable molecules: The composition of the plasma is therefore determined mainly by the recirculation and the wall association. This view explains the measurements under (1) and (2). The measurements with the H_2 (D_2) arc point to incomplete dissociation, leading to a marginal HD population. It may be worth noting that only the very good sensitivity of the CARS experiment makes the asymmetry detectable.

The essential importance of this view lies in the fact that the composition of plasmas of this type can be entirely determined by recycled stable monomers. Furthermore, dissociation of *all* basic molecules (in this case, H_2 and D_2) is necessary to obtain total mixing: Volume processes are not fast enough, as is indicated by the measurements under (3) and (4). Careful measurements using advanced diagnostics can thus lead to a better global understanding of plasma chemistry in general and of deposition and etching plasmas and plasma sources in particular.

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