

Diagnosics needs for understanding plasma assisted deposition

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Diagnostics needs for understanding plasma assisted deposition

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Abstract

The properties of the deposited materials and the deposition rate depend on the fragmentation processes of the deposition monomers in the plasma, on the plasma transport and on the processes at the surface. In order to optimize plasma deposition diagnostics are used to analyse the kinetic and transport processes in the plasma, which must clear up the role which the several deposition and etching precursors have in the layer growth mechanisms. In this contribution several diagnostic methods for the measurement of plasma quantities, radical densities and ion and radical fluxes are described. To guide the discussion of the diagnostics, including the required sensitivities, a crude overview of the various subprocesses of the plasma deposition process is given. Some typical results will be used to elucidate the merits of the various diagnostic methods.

1. Introduction

Plasma deposition and surface modification can be summarized as the result of plasma production, fragmentation of deposition and etching monomers, transport of the precursors in radical or ion form by diffusion or convection to the surface and surface processes as ad- and de-sorption, abstraction, deposition, cross linking [1]. If ions prevail then also the ion impact energy is important. Besides these primary processes also secondary processes as production of new monomers and etching gases (in particular hydrogen) and recirculation of these produced gases to the fragmentation zone may be important [2]. Further, the generation of particulate matter, not considered here, may complicate matters further [3]. The secondary processes, may on their turn may influence the primary plasma parameters and therefore the fragmentation of the seeded in monomers. Ideally one should measure all fluxes of ions, electrons, radicals, radical composition, and in addition keep record of the energy and photon flux. In practice this is an enormous task even for one particular deposition method, as e.g. a-Si:H, on which subject relatively much is published. However for a first assessment it may

suffice to obtain numbers for the electron (or ion) induced fragmentation (i.e. electron density), the transport of the radical and ion precursors, probably with a subdivision of radicals with low and with high sticking probability. In this contribution we will mention some illustrative examples: the use of H atoms for surface modification and SiH₄ fragments for a-Si:H deposition.

These illustrations relate to either in situ processing in RF or microwaves plasma or to a particular form of remote plasma treatment: the expanding plasma beam method. The latter offers the advantage that in this case the electron temperature is low and thus all fragmentation is ion or radical induced, rather than by electrons, so eliminating at least one complexity and the dependence on T_e . This limitation is however not essential and most methods are applicable in other methods, as long as sensitivity requirements are met.

2. Electron (ion) density and temperature

To evaluate the dissociating power of reactive plasmas it is essential to know the electron density. Here already the use of molecular components of the plasma offers complications: as the lifetime of plasma is typically 10^{-5} - 10^{-4} s and dissociative recombination rates are in the order of 10^{-13} m³s⁻¹ one should expect the molecular ion density to be maximum 10^{17} m⁻³. This value is only reached in the modern high density remote source approach; in the RF discharges they are typically one order of magnitude lower. (Note, that in atomic gases (argon) the densities are higher, but that is not relevant to our study even though many measurements are reported for argon). Hence we are faced with low electron densities and most studies rely on probe measurements [4]. However also these are problematic: it requires the knowledge of the dominant ion mass, and electron temperature, deposition on the probe may occur, negative ions may be present and in the case of RF compensation of the fields is necessary. An unambiguous method is the use of the classical microwave cavity detuning method [5]. This method has the advantage that it measures the electron density, which (also in the presence of negative ions) is the most relevant quantity as it determines the net production and the fluxes to the substrate [6]. Combined with photodetachment [7] the method offers very elegantly also a spatially resolved negative ion density measurement and thus also the positive ion density. It should be worthwhile to compare this method with probe measurements without and with photodetachment, as still some debate exists concerning the probe results interpretation. The microwave method is restricted to low density plasmas, $n_e \leq 10^{16}$ m⁻³.

For higher electron densities 2-8 mm interferometry may offer a possibility, with the disadvantage of spatial integration and of access requirements of the windows.

The preferred method is Thomson scattering [8], which delivers spatially resolved electron density and electron temperature (typically $n_e > 10^{17} \text{ m}^{-3}$) and also the neutral density by Rayleigh scattering. The sensitivity of the latter depends very much on the quality of straylight suppression, which apart from the laser and detection makes the method relatively expensive. Another disadvantage, not much addressed is the unavoidable photodetachment of negative ions, which may make the measurement an overestimate of the electron density. Typical sensitivities are $n_e = 10^{17} \text{ m}^{-3}$, $n_a = 10^{20} \text{ m}^{-3}$ and the accuracy for T_e is 10% at the common value of $T_e = 3 \text{ eV}$. These values can only be reached if efficient straylight suppression is possible [9].

For in situ processing the value of T_e must be known with high accuracy, as the ionization and dissociation rates depend exponentially on this quantity, apart from the linear dependence on n_e and the density of the primary neutral. The required accuracy can however never be reached even with Thomson scattering. In fact a prediction on the basis of the mass balance of electrons, which balances the production of electrons by ionization with the loss by diffusion and/or convection is usually more precise than measurements can provide. This can be illustrated by calculating T_e (in eV) for a specific value of the pressure and two values of the electron loss time: 10^{-5} and 10^{-4} s, assuming a Maxwellian energy distribution and an ionization rate $k_{\text{ion}}(T_e) = k_0 \cdot \exp(E_0/T_e)$ for simplicity:

$$E_0/T_e = -\ln(n_0 k_0 \tau_n) \approx \ln(100) - \ln(1000) \approx 5 - 7$$

With typical values for $k_0 = 10^{-14} \text{ m}^3 \text{ s}^{-1}$ and $n_0 = 10^{21} \text{ m}^{-3}$ and the specified values for $\tau_n = 10^{-4}$ or 10^{-5} s. So even this very crude "analysis" gives us already a prediction with a precision of $\pm 20\%$ without any measurement, which may be already better than probe measurements in RF molecular plasmas. Hence it is always better to use a classical spectroscopic method to obtain an exponentially sensitive value for T_e . In other words it is usually essential to complement accurate n_e measurements with a method, which apart from the value of $n_e n_0$ gives directly the production power of the discharge. Therefore just a combination of advanced scattering techniques with an absolute determination of emissivities of atomic (and molecular) lines is the best approach, whereas usually one does either scattering or the classical spectroscopy. The interpretation of emission and absorption spectroscopy even for atomic gases requires a priori knowledge of the electron density, as depending on n_e other collisional radiative regimes exist with different n_e dependences (for ionizing plasmas) [10]:

Corona: $n_p/g_p = n_0/g_0 n_e k_0^{\text{exc}} \exp(-T_e/E_0)/A_p$

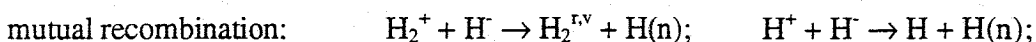
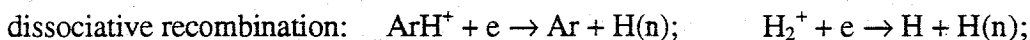
Excitation Saturation: $n_p/g_p = n_0/g_0 k_0^{\text{exc}} \exp(-T_e/E_0)/k_p^{\text{deexc}}$ valid for $n_e > 10^{19} \text{ m}^{-3}$

For even higher electron densities (and/or higher levels considered) the Saha density applies, but for the present discussion this is not of interest.

If a low lying radiating level is considered the corona model applies as long as $n_e < 10^{18} \text{ m}^{-3}$ which is commonly the case for processing plasmas, even in the high density case. Hence for ionizing plasmas, i.e. in RF plasmas, or in the source region of remote plasma treatment, a combination of Thomsonscattering and emission (or even better absorption) spectroscopy (is needed in combination with Rayleigh (or Raman) scattering to determine the neutral density) is the best approach to find the net production of radicals and ions by electron induced dissociation and ionization.

3. Use of emission (and absorption) and molecular processes

A natural consequence of the above analysis is that emissivities can be used to estimate the various ground state densities in actinometry [1,4], provided that there are no competing populating mechanisms of the considered e.g. atomic levels. This assumption is usually justified for elements with a high excitation threshold as noble gases. For atomic radicals like H atom this may not be correct, as dissociative recombination and mutual recombination may populate excited atomic levels very efficiently [2,11]:



Molecular ions dominate, if the ionization degree is not too high and thus these processes will influence the excitation of radicals even in ionizing plasmas, in which electron excitation is effective as well. If the source gives dominantly atomic ions, then molecular ions will still be produced in the downstream section by the process of charge exchange, if exo-thermic:



in which process charge is transferred to a molecular ion. Commonly charge exchange is slower than dissociative recombination and is thus rate limiting for $n_e/n_{\text{mol}} > 10^2$. Therefore it is better to measure the abundances of atomic and molecular radicals by other methods, as the later to be discussed UV absorption spectroscopy, TALIF, Raman and CARS methods, or by mass spectrometry.

Let us now turn to recombining plasmas (passive plasmas), downstream from the ionizing part, closer to the substrate, in the remote source approach. Here there is no existence demand on the electron

temperature, which is lower, depending on the nature of the downstream expansion process from the source. In this case electron excitation is much weaker or even absent and line radiation may be dominated by the above described sequence of charge transfer dissociative recombination processes (and mutual positive/negative ions recombination if negative ions are formed). The abundancies of the molecular ions (and of negative ions) are small, even though they are important as intermediate particle in the dissociation sequence. So actinometry and accurate T_e measurements are disputable here. For atomic radical abundances one has to resort to other methods, and as far as T_e is concerned, the precision of probes and certainly that of Thomson scattering is more than sufficient as no exponential processes are present. As an example in fig. 1 results [12] on n_e , and n_{Ar} , by Thomson and Raleigh scattering are shown of an expanding atomic plasma from a thermal cascade arc source for pure argon and argon admixed with small percentages hydrogen. From these results it is evident that the molecular hydrogen, which results from wall association of the atomic hydrogen from the source is very efficient in the destruction of electron density, even though the partial density of the resulting molecular hydrogen is relatively small (0.7 resp. 1.4 % of the total neutral density of 10^{21} m^{-3} at the pressure of 40 Pa and $T_h = .25 \text{ eV}$) [12].

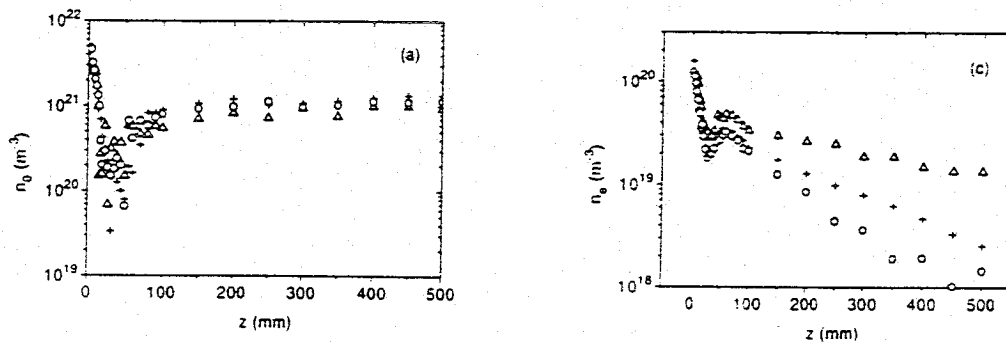


Fig. 1 Electron density and neutral density of an expanding plasma for pure argon, and for 0.7% and 1.4% H_2 in argon as measured by Thomson and Raleigh scattering. Conditions: $I_{\text{source}}=45\text{A}$, flow=58 scc/s, $P_{\text{vessel}}=40 \text{ Pa}$ [12].

In recombining plasmas there is a total other use of classical spectroscopy: the emitted light of molecular fragments may now be a token of the exchange and dissociative recombination processes and is thus in combination with n_e measurements a very useful tool, commonly underestimated in the analysis of deposition plasmas. In this respect it is even better to use LIF or absorption spectroscopy to measure the density of low lying states, as in many instances the recombination energy is only sufficient to populate these states. If a laser is used (e.g. a diode laser as is easily possible for Ar (4p-4s) and becomes feasible for H_α) one can at the same time obtain the flow velocity and the

temperature of the considered neutrals. Also ion energies have been measured this way ($\text{Ar}^+(4p-3d'')$) and ion acceleration in the sheath could be measured this way [13].

Other less elaborate methods to determine ground state densities rely on the presence of high energy electrons, either by local RF excitation or by the use of an electron beam. Then the same procedure as for ionizing plasmas applies, as in this way a small local ionizing plasma is created in the recombining background. The electron beam method is to be preferred, as the electron energy can be controlled. Another disadvantage of (RF excited) probes is that they may disturb the flow pattern.

4. Molecular and radical abundances

In order to calculate the radical fragments the monomer densities need to be known. In a first approximation one can assume that the molecular abundancies are equal to the partial densities in accordance with the original flows. In this model full recycling of the original monomer gases is assumed and equal pumping strength for all gases. The model relies on the assumption that the residence time is much longer than the time constant of one recirculation and also much longer than the time needed for wall association of dissociated fragments. If all these requirements are met, which usually is the case, this may still be an oversimplification. The reason for the deviation from the partial pressure picture is threefold: radicals may be lost by deposition and in deposition the ratio between e.g. Si and H in the deposited layer is much larger than in the original monomer SiH_4 : 10:1 instead of 1:4. The second reason is that desorption of molecules may occur in a different form than the original monomer, in e.g. CH_4 plasmas C_2H_2 and C_2H_4 may be generated. The third reason may be etching, giving also rise to new monomers. As a pertinent example of these processes H_2 will always be formed in deposition plasmas of hydrogen containing monomers. At the same time this conversion of original monomers to new ones is a sign of chemical activity: for new monomers to be formed, the original monomers must be fragmented to guarantee sufficient dwelling time at the surface to react and form new monomers, which desorb. In this picture also the effective sticking probability must be taken into consideration, as well as the probability for deposition or desorption reactions at the surface. In other words, it is even very useful to know the actual composition of neutrals, besides the composition of the radicals, which we will discuss later. There are several methods to determine the composition of stable monomers, of which we will mention Fourier Transform Infrared Absorption Spectroscopy (FTIRAS), mass spectrometry (MS), Raman Scattering (RnS), Coherent Anti-Stokes Raman Scattering (CARS), and its resonant form

(RECARS), whereas also the earlier mentioned electron beam excitation with fluorescence could be used to this purpose. UV absorption spectroscopy can not always be employed as many stable monomers are not active in this respect. We will shortly mention some results of the first five methods.

With FTIRAS specific resonances are monitored of molecules and radicals in the absorption spectra with typical resolution of better than 1 cm^{-1} [14]. With single or double pass arrangements sensitivities of 10^{18} m^{-2} can be reached, which is equivalent to .1 monolayer on a surface. For typical pressures in deposition plasmas of $> 10 \text{ Pa}$ this provides sufficient sensitivity to analyse the abundances of e.g. C_nH_m or Si_nH_m molecules, see fig. 2 for a measurement in CHF_3 [14]. As the resonances overlap of several molecules, it is only partly applicable. Also radicals can be detected in this way, at least in principle, but again resonances overlap may make this difficult and the densities are usually (much) less than those of the stable monomers. With high resolution IRLAS with diode laser detection of radicals is possible [15] as will be mentioned later.

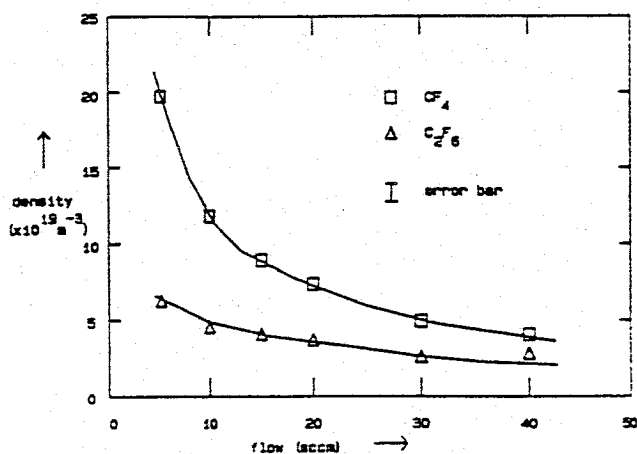


Fig. 2 Densities of generated monomers CF_4 and C_2F_6 in a "pure" CHF_3 RF plasma ($P=80\text{W}$, $p=13.3 \text{ Pa}$) as function of the flow measured by FTIRAS [14].

Mass spectrometry is a very powerful method with high sensitivity. Here the ionized fragments of the molecule are analysed with mass spectrometry, and the main problem is the need to disentangle the various fragmentation patterns of the molecules present in the discharge. Improvement can be achieved by Appearance Potential Mass Spectrometry (APMS) [16], in which the resulting ion abundances are measured as function of the potential of the ionizing electrons. Again radicals can be measured this way, if they have a lower ionization potential than the original monomer.

5. Densities of (general) monomers

Raman Scattering provides a local and absolute measurement of the various molecular constituents of a processing plasma. In fig. 3 a nice example is shown of such a measurement [17] in a CH_4 deposition ECR plasma at a pressure of 50 Pa, i.e. at a total density of 10^{22} m^{-3} .

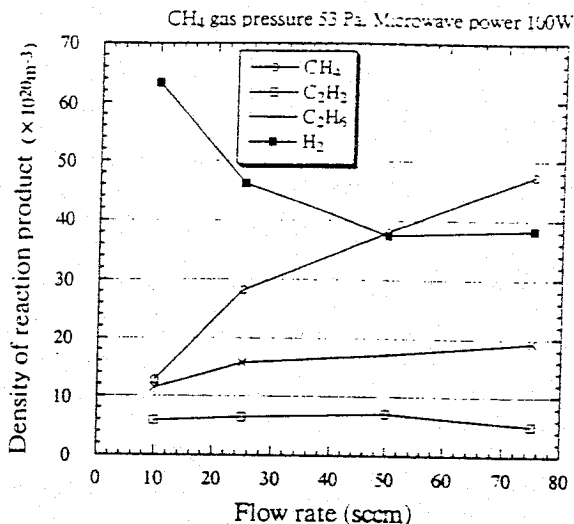


Fig. 3 Densities of stable C_nH_m monomers of a "pure" CH_4 (ECR) plasma [17] measured by Raman scattering. $P=100 \text{ W}$, $p=53 \text{ Pa}$.

Despite the limited sensitivity of this method one can clearly see the conversion to other monomers, in particular H_2 , but also to C_2H_2 and C_2H_4 . This process becomes more efficient at a low flow/pressure ratio, i.e. for high recycling conditions (long residence times) and it of course increases with power. CARS is the coherent version of Raman scattering with the advantage of a coherent detection signal. Therefore it is more sensitive than Raman scattering. However the method requires a very elaborate aligning and high quality laser beams of large power and is thus more demanding.

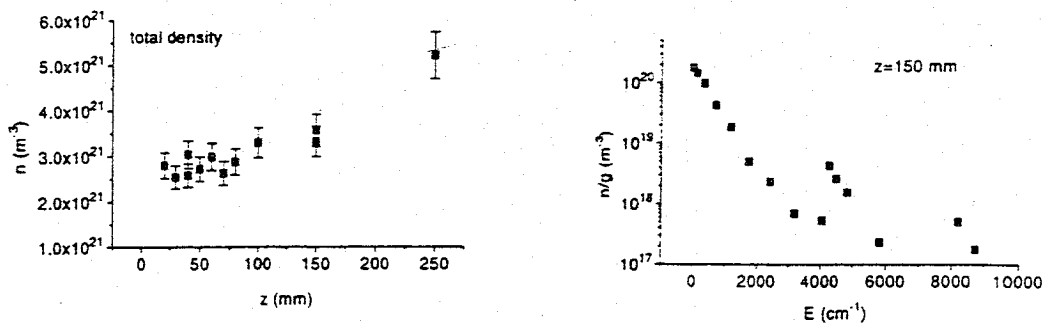


Fig. 4 $\text{H}_2(r,v)$ densities in an expanding plasma in pure H_2 at $z=15 \text{ cm}$ from the source measured by CARS. Also shown is the axial total H_2 density as function of the distance from the source [18]. $I=45 \text{ A}$, $\Phi_{\text{H}_2}=58 \text{ scc/s}$, $P_v=40 \text{ Pa}$.

To illustrate the possibilities with CARS we will shortly describe some experiments with Ar/H₂ and H₂/D₂ mixtures [18]. In fig. 4 results obtained from the CARS spectrum are shown for a position of $z=0.15$ m from the cascade arc source [18], which delivers mainly dissociated fragments, i.e. H atoms and atomic ions. Still at the position of the measurement the main H containing particle is the H₂ *molecule* produced in wall association of the H atoms. With the measured temperature from the low lying rotational lines one can determine the partial pressure of H₂. Also shown in fig. 4 is the measured dependence of the total H₂ density, which is in accordance with the pressure. Note, that this measurement does not show high densities near the source, which indicates substantial dissociation in the source. In Ar/H₂ mixtures the H₂ density appears to agree with the prediction of the full recycling model (i.e. $p_{H_2} = (\Phi_{H_2}/\Phi_{total}) p_{total}$) within the estimated absolute accuracy of the CARS method.

Note also the overpopulation of the higher rotational and vibrational states in fig. 4; this result indicates a possible specific role of even higher rotational states if this trend would persist. As the statistical weight of rotational states increases as $2J+1$ a significant fraction of the total density is in the excited states with internal energies in excess of 1 eV. As these densities may outnumber the densities of hydrogen atoms further analysis is warranted [18].

The effectivity of recycling is demonstrated in a second experiment [19], in which H₂ and D₂ was used as source gas (again effectively dissociated in the source) and the formation of HD was monitored by CARS. It appears that the composition of the downstream vessel plasma is fully determined by the recycling: using the densities and the rotational temperatures the partial pressures of HD, H₂ and D₂ (the latter determined by subtraction from the total pressure) are as 2:1:1. This result is expected for full recycling as there are two chances to form HD for one to form H₂ or D₂. Also in this experiment there are signs of overpopulated high rotational states, but again the sensitivity (though very good for CARS) was insufficient to measure these.

VUV absorption spectroscopy would give an alternative; it is a line integrated measurement, and at moderate densities it becomes unusable, because of self absorption. However for high rotational states, which may be peaked in the centre of the plasma beam and are less dense, the high sensitivity is just an advantage. However again the laser requirements are heavy [20].

6. Radical measurements

The most difficult problem is the measurement of radicals; some successes have been made, but rarely densities of more than one radical is determined. We will summarize the results of one such study by Tachibana, Kono et al and at the same time mention the employed methods. The SiH_3 radical was measured by diode laser infrared absorption spectroscopy, the high resolution equivalent of FTIRAS. The method requires a diode laser system and requires knowledge of the rotational spectra. With care an absolute measure of the radical density can be obtained. The SiH_2 radical density was measured by LIF (or absorption) in the visible as was the SiH density and the Si atom by UV absorption. It appears that in the employed RF plasma SiH_3 is the most abundant radical, but still low in density. In these plasmas with power densities of $.1 \text{ W/cm}^3$ the SiH_3 density it is typically 10^{18} m^{-3} i.e. .1% of the SiH_4 density, whereas the other radicals Si, SiH , SiH_2 are at least two orders of magnitude lower [15,21]. The radical densities are likely to be higher in experiments, in which the deposition rates are higher, as commonly the SiH_3 radical is assumed to be the deposition precursor. Still radical abundancies, in particular SiH_3 (and CH_3 in the CH_4) case are not easy to measure. RECARS [22] has been used also to measure CH abundancies in microwave deposition; also these measurements showed low abundancies for this radical.

Radicals can also be measured by Appearance Potential Mass Spectrometry [16]. In this case the sensitivity for radicals is enhanced by using electron energies with energies below the ionization threshold of the monomer, but above that of the investigated radical. Again the low abundancies of radicals provide a problem.

To finish the discussion on radical measurements we will summarize the applicability of TALIF to measure atomic radical densities with a large excitation threshold. In this method *two* UV photons produce an atom in a radiating excited state and the excitation is monitored by observation of the fluorescence. Like in LIF information on the systematic velocity and the temperature can be obtained. The method can be calibrated by titration [23]. An example is shown in fig. 5 from recent work by Brinkman, Döbele and Boogaarts et al. [24] on atomic hydrogen in similar conditions as the earlier mentioned CARS work. Clearly the fast expansion of the hydrogen atoms is seen leading to low densities in the subsonic expansion region. Also it appears that the sensitivity of the method is limited to 10^{18} m^{-3} . For lower densities VUV absorption may again provide an alternative.

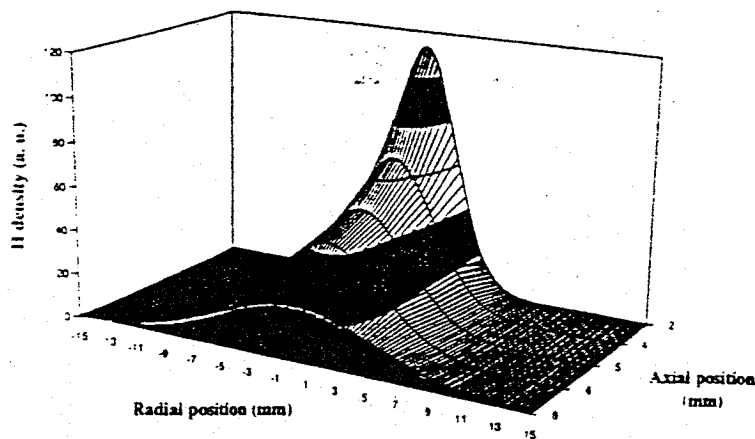


Fig. 5. H-atom density in a H_2/Ar expanding plasma as a function of the distance from the source. An estimate for absolute density based on the assumption of full dissociation in the source would be $1 \text{ a.u.} \triangleq 10^{19}/m^3$. $I=40 \text{ A}$, $\Phi_{\text{argon}}=50 \text{ scc/s Ar}$, $\Phi_{H_2}=8 \text{ scc/s}$, $p_v=10 \text{ Pa}$ [24].

7. Conclusion

The general conclusion is that in many cases a combination of scattering techniques with more classical methods may provide the best clue to obtain the essential information on particle densities, production efficiency and on the production of new monomers. The latter may give an important clue to the fragmentation efficiency, as dissociation of the original monomers is an essential step. By knowing the fluxes, one can attempt to find the dominant processes at the surface and so optimize the growth of thin layers in plasma deposition.

Acknowledgement

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