Plasma processing and chemistry*

Daniel C. Schram

Eindhoven University of Technology, Department of Physics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract: Plasma deposition and plasma conversion can be characterized by five steps: production by ionization, transfer of chemistry to precursors, transport of radicals to the surface, surface interactions with deposition, recirculation and generation of new monomers. For very fast deposition, large flows of radicals are needed and a regime is reached, in which monolayer coverage is reached in a very short time. Such large flows of radicals can be obtained by ion-induced interactions, as the C2H radical from acetylene for a-C:H deposition, or by H atom abstraction as the SiH3 radical from SiH4 for a-Si:H deposition. These radicals with intermediate sticking coefficient are advantageous as they are mobile and have a finite dwelling time at the surface. By such a pure radical mechanism, good layers can be formed with very high growth rates, if large radical fluxes can be reached. This regime of high fluence is also interesting for conversion, of which ammonia formation from hydrogen and nitrogen atoms is given as an example. These new approaches offer new possibilities for further development of the field in close connection with surface science, catalysis, and materials science.

INTRODUCTION

Plasma chemistry, plasma deposition, and plasma surface modification offer new challenges to materials science and chemistry. The relatively large fragmentation of injected monomers, the high temperature of the plasma medium, and chemical energies of radicals give principal advantages to plasma methods [1–3]. New materials are possible, the freedom of choice in constituents is unlimited, and material properties such as crystallinity and morphology can be “chosen”. The low material content and high fragmentation make plasmas relatively safe and environmentally friendly. The problems with plasmas are two-fold. First, it is difficult to achieve large fluxes, and, thus, high process rates and plasma treatment on large scale need further advance [4]. Second, as plasmas are far from thermodynamic equilibrium, it is not easy to “design” a result. Fragmentation patterns are difficult to predict, recirculation and wall production of new monomers may partially replace injected monomers [5], and surface interactions may vary with the radical fluxes, which on their turn may be altered by the changing surface processes. Models have been designed, which may explain what is observed [6–8], but they cannot always be used to predict new routes. Therefore, it is useful to analyze the problem of plasma deposition and/or catalysis in a principal way and to inquire how far one can get with a general picture.

Plasma processes can be subdivided into five subsequent steps [5], which either can take place in the same volume, or can be geometrically separated as in remote source processing. In the latter case, they may be better distinguishable, as indicated in Fig. 1, but these steps are always there.

1. Creation of primary plasma, i.e., electrons (and ions) in the production volume I. This ionizing plasma can be atomic, as in remote source operation, or molecular, as in in situ processing.

2. Transfer of primary chemistry to secondary chemistry, i.e., dissociation of injected monomers in the recombining plasma from the source. Chemically active radicals and/or ions are formed, which may be characterized by their reactivity and sticking probability on the growing film: “hard” radicals with a high sticking coefficient (>0.5), “intermediate” radicals with intermediate (0.05–0.5), and “soft” radicals with low sticking coefficient (<0.05).

3. Plasma surface interactions of arriving radicals with a surface lead in first instance to the formation of a chemically bounded surface layer and thus to a (nearly) totally passivated surface. Subsequent-arriving hard radicals will still stick to this surface, whereas intermediate radicals may diffuse across the surface. By finding a vacant site or by reaction they may contribute to deposition and cross-linking. Alternatively, they may abstract, e.g., atomic hydrogen, leading to an open site and desorption of a molecule, or they may reflect as soft radicals. Desorbed molecules can be chemically active, as is clear from the production of ammonia in the presence of atomic hydrogen and nitrogen [9].

4. Nearly always there is recirculation and new molecules produced in the volume or at the wall will mix with injected monomers [5]. We will distinguish the “forward kinetics” volume II with the plasma from the source and the “background” volume III, in which recirculation takes place.

5. Clustering of (recirculating) monomers, radicals, and ions; nucleation and formation of dust. In this contribution, we will not treat this aspect; we mention, though, the possibility of cluster formation by ion–ion association in charged recirculating eddies [10,11].

The various physical processes can be characterized by time constants [5], production time $\tau_{\text{prod}}$, loss time $\tau_\text{l}$, transit time $\tau_\text{tr}$, circulation time $\tau_\text{circ}$, residence time $\tau_\text{res}$, etc. These time constants can then be compared to a coverage time $\tau_\text{cov}$, i.e., the time needed to cover the surface with one monolayer. It can be shown that plasma chemistry, done for a wide range of parameters, can be classified according to the ordering of these time constants. If, for example, the coverage time is much shorter than the circulation time then we deal with a high radical flux situation. Surface reactions may then have additional features as compared to a very low flux situation, when surface coverage takes many residence times. Possible nonlinear processes at the surface by weakly bound radicals could become important at high flux conditions.

We use for illustration the remote source approach of expanding plasmas, in which method the steps are well separated. The source delivers a large ion or a radical flow, chemical transfer reactions
occur in a flowing recombining plasma of low-electron temperature, and ion energies in the sheath are small, all aspects which facilitate the analysis.

**PLASMA PRODUCTION AND PLASMA SOURCE**

The first step in plasma processing is the production of plasma by ionization. This can be in the deposition monomer mixture (e.g., SiH₄ and H₂ for a-Si:H deposition) [3]. Alternatively (as in remote plasma processing), primary ions of a carrier gas can be produced, which can then later be used to transfer excitation and ionization to monomers to produce deposition precursors [4]. Some general statements concerning the electron temperature in the source and the required power to produce the desired plasma flow can be made from the mass and energy balances as nonequilibrium constraints [5]. The mass balance

\[ \int_{\text{Vol}_I} k^{\text{ion}} \cdot n_e \cdot n_o \cdot d\text{Vol}_I \equiv \frac{n_e}{n_o} \cdot \text{Vol}_I \]

needs to be made up for the active volume, Vol₁, where dissipation by DC, RF, or microwave power heats up the electrons, until sufficient electrons have enough energy to compensate the losses by ionization \( (k^{\text{ion}} \) is ionization rate, and \( n_o, n_e \) are neutral and electron densities). The mass balance equates the electron and ion production by ionization \( (\tau^{\text{prod}}) \) to the loss \( \tau_n \) by diffusion, convection, attachment, and recombination. In remote plasma processing, commonly the loss by convection is dominant, which gives us a time estimate of \( \tau^{\text{prod}} = \tau_n \propto l_s / c_s \), in which \( l_s \) is the source length and \( c_s \) the acoustic velocity. It appears that the electron production time constant, \( \tau^{\text{prod}} \) is indeed between a few \( \mu s \) for light gases to a few tens of a \( \mu s \) for heavy carrier gases. The mass balance simply boils down to equating the production rate to the loss rate \( k^{\text{ion}} n_o = (\tau^{\text{prod}})^{-1} \)

\( = (\tau_n)^{-1} \). Apparently, the mass balance teaches us that a minimum (effective) electron temperature is needed in the source, which depends logarithmically on dimension, loss time, and pressure. This does not need to be a Maxwellian energy distribution; at higher ionization degrees it will. Typically, it is 4 eV at low pressure to 1 eV at high pressure [5].

The energy balance equates the dissipated power integrated over the active volume to the energy carried away by the produced plasma flow, multiplied by a correction factor \( \xi \) to take care of other losses. This factor \( \xi \) varies from 10–30 at low pressure to 2–3 at high pressure for noble gas as argon. Apparently, plasma production is the most effective at high pressure, by virtue of the then higher electron density. Typically, a minimum of 30 eV per ion is needed, which means that for 1 kW of power \( 2 \times 10^{20} \) ions/s result. This would be sufficient for a deposition rate of 100 nm/s over 1000 cm². It appears that thus the efficiency in the source is a key design parameter for fast plasma processing at moderate power levels. Another important item is the gas efficiency. With thermal plasma sources, 10 % ionization can be achieved and only then large ion flows are possible with still acceptable pumping systems.

We will use here the expanding thermal plasma beam system for illustration of the dynamics of plasma deposition [4,5,12]. This remote source approach uses a thermal plasma, a cascade arc to produce the primary plasma. It operates at (sub)-atmospheric pressure, can handle large flows (typically 50–100 scc/s, 1 scc/s \( \equiv 2.5 \times 10^{19} \) /s) at moderate arc currents and power levels and produces a 5–10 % ionization degree plasma in argon. The ion flow is thus typically 2–10 scc/s (or 10–40 A equivalent), which is more than sufficient to provide for the downstream chemistry even at high rates.

The source can also be operated in some molecular gases, like hydrogen or nitrogen or a mixture. Then the main chemical species produced are the hydrogen or nitrogen atoms, rather than (atomic) ions. The reason is that even in nearly fully dissociated flows enough molecules occur to destroy ions by a sequence of charge transfer and dissociative recombination [13,14]. Hence, the source has to be used either as an ion source or as a hydrogen atom source. The atom flow produced in an argon hydrogen mixture corresponds to roughly 10 % dissociation in the arc (2 scc/s for a 10 scc/s H₂ in 55 scc/s argon). Whether this is due to incomplete dissociation in the arc or defocusing effects in the expansion is still unclear. This system is, thus, less effective for hydrogen atoms than for argon ions in pure argon.

A last remark in this section concerns the relation between ionization and dissociation. It is a general belief that dissociation is much easier than ionization and that this is the reason for higher radical
densities than ion densities. This is, however, much less true than it seems. In fact, the dissociation is typically only a factor 3–10 more frequent than ionization. That radical densities may be larger is more due to slower transport than to more effective production. Moreover, weakly sticking radicals may reflect from the surface and for that reason build up to higher densities. As at the end the net radical flux to the surface needs to be produced it is sensible to calculate the radical production rather than the densities. This radical production by dissociation can roughly be related to the ion production by ionization, which in turn can be related to the dissipated power in the source. This gives a fast estimate for the chemical energy stored in dissociation. A consequence of this observation is that the ratio of \( n/\tau \) is the important quantity [5] and that in many cases it is of the same order for both hard radicals with low \( n \) and soft radicals with large \( n \).

PLASMA EXPANSION AND CHEMISTRY TRANSFER

The next step in plasma processing is conversion of the primary plasma chemistry to the deposition precursors and at the same time transport of these to the treatment volume and surface. Here comes another virtue of plasma production at high pressure: the expansion [12], first supersonic and after a stationary shock subsonic, guarantees a fast transport with a short transit time, \( \tau_{tr} \), typically \( 10^{-4} \) s. The plasma exits sonically out of the source, then accelerates in the expansion, and the densities decrease quadratically with distance from the source \( 1/z^2 \). The temperature decreases too and quasi-adiabatically (with a lower \( \gamma \)). When the stagnation pressure becomes of the order of the background pressure a stationary shock occurs. The position of this shockfront \( z_m \) can be given in terms of flow, \( \Phi \) in scc/s and pressure, \( p_{\text{back}} \) in Pa; it depends weakly on the mass number \( A \) and on the source temperature, \( T_\text{\text{\hat{}}} \sim 1 \text{ eV} \) [12]:

\[
z_m = 0.02 A^{1/4} \Phi^{1/2} p_{\text{back}}^{-1/2}.
\]

The radial extent of the shock front is roughly equal to \( z_m \), as the expansion angle is roughly 45°, similar to a gas expansion. Also, no significant ion loss occurs due to three-particle recombination; it does lead to population of excited neutrals and thus to line emission, but it is insufficient for recombination. The light observed is due to this line and continuum emission, both being a sign of the presence of ions [14]. It is different from light emission in active plasmas, in which most light stems from excitation by electrons from ground-state neutrals.

This simple picture changes drastically in the presence of molecules, in particular \( \text{H}_2 \). If only a small fraction of the argon gas is replaced by hydrogen, then most light disappears and the remaining turns red, due to \( \text{H}_\alpha \) Balmer emission. Even though in the source most hydrogen will be dissociated, the present small fraction of molecules causes charge transfer from the atomic argon ions to molecular ions \( \text{ArH}^+ \) or \( \text{H}_2^+ \). These ions on their turn dissociatively recombine to excited hydrogen atoms, causing the red light emission [13]. Note that also here light emission is a sign of ions (which recombine). The effect of ion loss by the combined effect of charge transfer and dissociative recombination is clear from the much shorter light plume in molecular seeded expansions.

The next question is where the hydrogen molecules come from if they were fully dissociated in the source. The reason is quite simple: any hydrogen atom will eventually re-associate with a wall-adsorbed atom if it arrives at the wall [14]. As recirculation is nearly always present and the residence time is much longer than a recirculation time, most of its time the hydrogen is present in molecular form. Hence, downstream of the shock the molecular density will be higher than the atom density, even with an atomic hydrogen source.

Ions start to recombine in the barrel shock before the stationary shockfront. Thus molecular hydrogen must enter the barrel shock from the side, where it was supposed to be closed. This is due to the fact that the mean-free path, \( \lambda_{\text{mfp}} \) is of the order of the shock dimension. Equating \( \lambda_{\text{mfp}} \propto \sqrt{z_m} \) gives the following product of flow \( \Phi \) (in scc/s) and background pressure \( p_{\text{back}} \) (in Pa), below which the anomalous inflow is to be expected: \( \Phi \cdot p_{\text{b}} \equiv 10^3 \) [scc/s·Pa]. At this critical value, the inward flow from the periphery can be as large as the flow from the source. This picture is supported by detailed radial and axial velocity distribution measurements, in argon [15], in argon hydrogen mixture [16], in pure...
hydrogen [17], and in nitrogen [18]. It is a very beneficiary effect for mixing of injected (and produced) molecules with the primary chemistry from the source.

The last unexpected complication is the so-called mass defocusing [12]. If a source delivers atomic hydrogen in an argon plasma, the hydrogen atoms (and ions) are scattered out off the expanding plasma. The reason is simple: the light hydrogen atoms tend to be accelerated but are hindered by the heavier and thus slower argon atoms and ions. This in turn will lead to a diffusion-like behavior of the hydrogen atoms in the argon-dominated flow. This effect is detrimental for processing, as in nearly all cases this leads to a very serious loss of atoms in the forward beam. As these atoms will probably reassociate at the wall near to the source exit, these are lost for the downstream chemistry. A large exit velocity, thus longer laminar expansion, may help to minimize these losses of radicals by this effect.

CHEMISTRY TRANSFER AND PRODUCTION OF DEPOSITION PRECURSORS

The next step is the transfer of chemistry from the primary carriers (argon atoms or H atoms) to the injected and mixed-in monomers like C2H2 or SiH4 to produce deposition precursors. These monomers are introduced by, for example, an injection ring in the background, where these mix with the recirculating gas. The partial pressures in the resulting mixture are proportional to the partial flows, corrected for consumption or production. The resulting mixture mixes in the plasma beam in the vicinity of the shock front, and radicals are produced. The diameter of the forward-flowing subsonic plasma is roughly constant after the stationary shock-up to close to the substrate. A recirculating eddy fills the space in the periphery between the forward beam and the vessel wall (cf. Fig. 1). If the shock structure is partially transparent the monomer gas mixes there with the primary plasma, which contains either argon ions (with pure argon in the source) or hydrogen atoms (with Ar/H2) as chemical agent. Both routes are used: the ion route for a-C:H deposition and the radical route for a-Si:H deposition. The difference in strategy brings us to the next discussion item: which radical is to be preferred for good material deposition and is it possible to select this radical. There is a general belief that radicals with an intermediate sticking coefficient are preferable. In this picture [4,5,19], hard radicals with a high sticking coefficient and chemical binding energies, will show no mobility at the surface. Soft radicals with very low coefficient and physical binding energies will not stay long enough at the surface to lead to deposition. The preferred “intermediate” radicals with intermediate energies can be reached with ions in the C2H2 case and with H atoms in the SiH4 case. We will discuss both cases and use them to illustrate the various dissociation routes.

Deposition of a-C:H

The deposition of the amorphous hydrogenated carbon is an important example. It is based on dissociation of hydrocarbons, and the resulting layers can be polymer-like or hard and dense. It has been shown that the hardness is directly related to the index of refraction and to the density of the film. We will first discuss the acetylene case. If acetylene is mixed into the primary argon plasma the first reaction is a charge transfer, followed by dissociative recombination [20]:

\[
\text{C}_2\text{H}_2 + \text{Ar}^+ \rightarrow \text{C}_2\text{H}_2^+ + \text{Ar} ; \quad \text{C}_2\text{H}_2^+ + e \rightarrow \text{C}_2\text{H} + \text{H}
\]

As a result, the C2H radical is produced, which is the preferred precursor in the amorphous carbon case. From the radicalization point of view this would be the optimum situation. As the first reaction chain has no significant side channels and the second is the most dominant, this is the case if subsequent reaction chains can be avoided. This calls for optimum loading [20]: at each primary plasma current so much C2H2 needs to be injected that the primary ions are all consumed in the first reaction chain. If, however, low monomer flows are used at high ion flows, then subsequent reactions in a second or even third cycle of reactions produce C2 and CH and even C and C+, all hard radicals with a high sticking coefficient. Hard radicals have indeed been measured under these conditions [21–23] and also
the layer quality proves to deteriorate for low C\textsubscript{2}H\textsubscript{2} flows. If the monomer flow is increased to critical loading, the hard radicals disappear, C\textsubscript{2}H becomes dominant, and the layer quality improves considerably. At the same time, the deposition rate increases, because of the higher level of fragmentation, thus, higher rate. This improvement of quality with rate is even more global. In Fig. 2 the index of refraction is plotted against deposition rate for many conditions, not only for C\textsubscript{2}H\textsubscript{2} but also with other monomers, like CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and other primary gases such as argon, helium/argon, and xenon [23]. The increase of index of refraction with deposition rate is stunningly consistent. There is some effect of substrate temperature with higher values at higher temperature. Figure 2 also shows some points from RF deposition studies and from ECRH deposition both obtained from Von Keudell [24]. For these conditions, ion effects are important, and the relation between film density and rate is different. Thus, we can conclude that for the EPB deposition method, which is radical-rich and ion-poor and shows no ion energies, another, pure radical, mechanism can give good-quality results at much higher rates. It looks difficult to ascribe this to the dominance of C\textsubscript{2}H alone by the reasoning above, as this would apply only to C\textsubscript{2}H\textsubscript{2} injection and not for other feed gases. Therefore, we will first discuss the other monomer cases.

Figure 3 shows two infrared absorption spectra [25]: one for C\textsubscript{2}H\textsubscript{2} and one for CH\textsubscript{4} injection. In the first case, one observes only a reduction of the absorption at C\textsubscript{2}H\textsubscript{2} wave numbers if the plasma is switched on, which is partly due to the higher temperature and partly to depletion. However, in the CH\textsubscript{4} case, the methane peak nearly disappears and an acetylene peak appears. Apparently, under the relevant conditions (good loading) the methane is to a large extent converted to acetylene. Deposition takes place again from acetylene and thus C\textsubscript{2}H, however at lower rates as the produced H\textsubscript{2} leads now to a decrease of the argon ion flow from the source [26]. If the loading is critical, no hard radical as CH or C are produced in a secondary reaction chain. The main radical produced in the first charge transfer and dissociative recombination cycle are CH\textsubscript{3} and CH\textsubscript{2} radicals, both believed to be soft radicals [7]. These reflect from the substrate surface and enter the recirculating background, where they reside until they react in the volume or at the vessel wall. As the dwell time is long, many wall collisions occur, and there may even be enough time for three particle interactions in the volume. As also with other feed stocks such as C\textsubscript{2}H\textsubscript{4} or C\textsubscript{2}H\textsubscript{6} mainly C\textsubscript{2}H\textsubscript{2} is produced, it looks likely that the main production is at the peripheral wall. Thus, also for other monomers, the mechanism is through dominance of C\textsubscript{2}H, at least at high

![Fig. 2 Refractive index of hydrogenated amorphous carbon layers as function of deposition rate for the EPB method. Points are given for various precursors and for varying substrate temperatures taken from Letourneur [22–23]. The good overall correspondence suggests a pure radical mechanism, in which a high flux of radicals is advantageous. The points marked RF and ECRH, obtained from Von Keudell [24], refer to RF plasma and ECRH plasma deposition. In these plasmas, evidently, ions and ion energy play a role and the mechanism is different.](image)
feed rates. It is a clear example of a more general rule: new monomers are produced and need to be considered. This general rule means also that it is not essential to select the perfect precursor.

The improvement of material quality with increasing flow rate and thus deposition rate is thus partly explainable by a growing dominance of the $\text{C}_2\text{H}$ radical and diminishing influence of $\text{CH}$, $\text{C}_2$, and other hard radicals. However, why the improvement is even global is more difficult to explain. Two possibilities have been suggested. One is the decreasing influence of a polymerization contribution of unused $\text{C}_2\text{H}_2$ [27]. It appears that at very high rates (i.e., high arc currents and large monomer flows) the relative density of $\text{C}_2\text{H}_2$ decreases compared to the $\text{C}_2\text{H}$ density, the major deposition precursor. Another, more speculative explanation is that deposition is favored by the interaction of two physically adsorbed $\text{C}_2\text{H}$ radicals. On the fully passivated surface, a finite binding energy could temporarily bind the mobile $\text{C}_2\text{H}$ to the surface. If diffusion of these radicals would be fast enough, then two radicals could meet and react before they are desorbed. With a binding energy of 0.6 eV, a diffusion coefficient of $10^{-7} \text{ m}^2/\text{s}$, a flux of $10^{21}/\text{m}^2\text{s}$ would suffice to make this possible. This speculative explanation is appealing, as it would rely on high radical fluxes, fully passivated surface (thus, large atomic hydrogen flux), and probably the presence of negative charge, in connection with the binding energy. Note that all these aspects would be only realizable in plasma environment and that for plasma conditions a new surface physics might emerge.

**Deposition of a-Si:H with SiH$_4$**

Deposition of amorphous hydrogenated silicon is another important example. There is much interest because of application in solar cell, display, and other technology [3]. It gives us also an example of the preference of the radical route. Charge transfer of argon ions with silane produces mainly $\text{SiH}_3^+$, which dissociatively recombines in $\text{SiH}_2$ or $\text{SiH}$, both radicals with a high sticking coefficient. Thus, even in the first cycle hard radicals are produced and less favorable deposition results are expected. With the radical route abstraction by atomic hydrogen leads to the $\text{SiH}_2$ radical [4,6,8,19,28,29], which is an intermediate sticking coefficient radical. Indeed, more dense layers are observed if hydrogen is admixed to the source, causing the source production to change from argon ions to hydrogen atoms. The deposition rate is not so large as in the ion route, but this is presently attributed to the mass defocusing loss of hydrogen radicals and thus insufficient source strength. Still rates of 10nm/s are reachable with good material properties.

Mass spectrometry reveals that in the case of silane nearly only silane is produced, or in other words silane does not become depleted and the production of disilane is small. There are signs in the literature that the presence of unconsumed silane is beneficial (unlike the assumed detrimental presence of unconsumed $\text{C}_2\text{H}_2$ in the a-C:H case). This can be explained by reactions in the gas phase of $\text{SiH}_2$.
radicals back to SiH₃, or alternatively SiH₄ could help to reduce hard sticking radicals like SiH₂ to intermediate ones like SiH₃ at the surface. If disilane is used, similar deposition results are obtained, which is partly explainable by the very effective conversion of disilane to silane, cf., Fig. 5. The present view on the mechanism of SiH₃-induced deposition is that this radical leads both to vacant sites of the hydrogenated surface and to adsorption to these sites leading eventually to deposition [28].

Hence, increasing the flux does not disturb the balance between these two necessary steps. Again, one invokes a finite binding energy for the SiH₃ radical at the hydrogenated surface, so that it can diffuse until it finds a vacant site. Note that also here a reaction of two SiH₃ radicals diffusing at the surface becomes possible if the surface binding is significant, if the flux is large, and if the mobility is high and this forms another mechanism for growth on a fully passivated surface. It is clear that in the process hydrogen needs to be lost as the incoming precursors are hydrogen-rich and the layer contains at the end only roughly 10%. It is for this reason that for ideal material the substrate temperature needs to be chosen higher than in the case of RF plasma deposition. At the much higher rate in the EPB method, the thermal hydrogen desorption needs also to be higher. The question now is whether the deposition mechanism is so "physical", i.e., specified precursor and specified surface conditions. It is still possible that a more general "chemical" picture, with more relaxation at the surface would suffice. In that case,

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**Fig. 4** Left: deposition rate of a-Si:H as a function of H₂ admixture (argon flow 55 scc/s, arc current 45 A, SiH₄ flow 10 scc/s, p<sub>back</sub> 20 Pa). Also given is the contribution to growth by SiH₃ radicals, obtained by threshold ionization mass spectrometry (TIMS) and by cavity ringdown spectroscopy (CRDS) [28,29]. Right: index of refraction in IR and photoconductivity showing improving material density and electronic properties with H₂ admixture [19].

**Fig. 5** Densities of SiH₄ and Si₂H₆ (expressed as partial pressure) for SiH₄ injection (left) and Si₂H₆ injection (right). Conditions, see Fig. 4 [29].
even the presence of hard radicals may be less serious, which might make deposition of good material possible with the ion route at much higher rates, if one can realize still a relatively large unused SiH₄ fraction. As understanding of the mechanism may thus lead to new strategies, the next step in this field is to investigate in situ the surface processes under high radical flux conditions to obtain a full understanding of the deposition process.

CHEMICAL CONVERSION, PLASMA CATALYSIS

In discussing deposition we have already passed two examples of chemical conversion in the plasma: the synthesis of C₂H₂ from other hydrocarbons and the production of silane from disilane (and hydrogen). It has been argued that these new monomers are mainly produced at the wall of the auxiliary volume, where the plasma recirculates, not in the primary plasma beam. It can be argued that for the lower pressure range reactions at the wall are more probable than in the volume, in particular if three-body reactions are required.

This general argument is based on the following observations. First, it is assumed that 2 to 1 volume reactions as, e.g., SiH₂ + SiH₄ → Si₂H₆, are improbable. In the literature they are often taken as explanation of the observed small presence of SiH₂. However, if one assumes a required stabilization by a third particle, an observer: SiH₂ + SiH₄ + obs → Si₂H₆ + obs, the three body rate (≤10⁻⁴₃ m⁶/s) is too small for the reaction to be efficient. Two-body reactions, like SiH₂ + SiH₄ → Si₂H₄ + H₂, can explain the low density, but will not lead to a change in reactivity of the radical: Si₂H₄ is still a hard radical.

A similar argument holds for the association of N atoms. In the volume, only a three-body reaction is possible: N + N + obs → N₂⁺ + obs, in which actually N₂⁺ is produced in an excited state [9,30]. For the forward kinetics, the three-body rates are by far too slow for the pressure range around 1 mbar. But in the background recirculating volume it may in principle be possible, as there is more time. The probability of association will depend on observer density (N₂) and atom density. The N density on its turn depends on the effectivity of association. If volume reactions would prevail the N/ N₂ ratio would be in the order of the ratio of N atom life time and residence time, τₐ / τₑ. This leads in many cases to a conflict: if association is assumed to be important, [N] is low, which is in contradiction with the required high [N] to make the association effective. Therefore [5], wall association has to be assumed as the leading mechanisms in the lower pressure range. For high radical fluxes the wall is fully covered by a monolayer and thus passivated. Then the N density builds up in the volume, until it is so large that association reactions on the passivated layer become possible. In the case of H and N atoms combinations as NH₂ [9] could fill the role of passivation layer leading to the production of NH₃, N₂H₄, etc. at the wall, depending on the flux conditions.

Hence, the principle is to produce nondepositing radicals and to let them react at the surface to produce new monomers, which desorb. At fully passivated surfaces, the desorption of active nitrogen in the triplet A state or rotationally and vibrationally excited molecules becomes possible [31]. Hence, here may be unexplored possibilities at high flux conditions. The production of ammonia from a source with nitrogen and hydrogen atoms as feed stock is a pertinent example. The NH₃ density is measured with infrared absorption [31–32] and is shown to be most present in the periphery of the vessel. Apparently, the produced ammonia accumulates in the background and leads to a finite partial pressure. It is shown in Fig. 6 [32], in which the density of NH₃ is plotted as function of partial H₂ flow, that the production of ammonia is the largest at the stochiometric feed of N₂ vs. three H₂, pointing again to a chemical mechanism, likely at the surface. It can be seen as an example of plasma-activated catalysis, a promising new line of plasma physics.

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CONCLUSIONS

The process of plasma deposition and surface modification has been analyzed to consist of several steps. The efficiency of the source proves to be important to achieve high rates with good quality. Also, the transport from the source and the transfer of chemistry to the monomers needs to be efficient. Then high radical fluxes are possible, which permits successive reactions of weakly absorbed radicals at the fully passivated surface. It proved also that possibly other monomers can be produced, a fact which has to be considered in the explanation. It is shown that in the amorphous carbon case the use of ions to produce radicals is possible and dense layers are obtained at high rates. Similarly, for a-Si:H good intrinsic material has been deposited with also high rates. Both results could be connected with the dominance of “intermediate” radicals, with intermediate binding energy at a passivated surface. The production of ammonia by injection of N and H atoms has proven that new chemistry is possible at large fragmentation levels. It is concluded that plasma chemistry enters a new stage. New in situ diagnostics will bring clarity to possible new physical mechanisms, only made possible by the very high fluxes. This would provide also new opportunities for scientific collaboration with other fields, as astrophysics (expanding jets, plasma chemistry), surface physics (“new” surface physics in plasma), geophysics (chemical reactions), nanophysics, etc. This would also be fruitful for plasma chemistry and guarantee new challenges to come.

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