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Abstract. Processing plasmas often produce clusters, ranging in size from a few nanometers up to micrometers. Due to their negative charge, clusters are confined by the sheath electric fields until their mass enables gravity to pull them out of the discharge. Examples are discharges in SiH₄ or C₂H₂. Although there is agreement on the global aspects of the chemistry, details on many processes are lacking. This concerns attachment of electrons to large molecules, restructuring leading to a reduction of the hydrogen content, and the interaction between large negative ions and (excited) molecules, radicals, and positive ions of the parent gas. Results from a one-dimensional model for a radio-frequency discharge in SiH₄/H₂ will be used to illustrate the consequences of various assumptions regarding these basic steps in the chemistry.

For discharges in mixtures containing hydrocarbons the incorporation of C₂ groups in polycyclic aromatic hydrocarbons has been proposed as an additional mechanism for dust formation. This is the main process adopted in astrophysics. Also in Tokamaks the formation of carbonaceous dust is observed, caused mostly by the erosion of carbon containing divertor tiles and redeposited layers on plasma facing components. In case of detached operation the plasma in the divertor will be similar to that of a processing discharge, favoring homogeneous processes. In ITER this will be accompanied by hydrogen ion fluxes up to 10²⁴ m⁻²s⁻¹ and power fluxes up to 10 MWm⁻², leading to evaporation of wall material. Here we will discuss the chemistry in these situations (processing discharges and divertors), indicating open questions regarding cluster formation.

INTRODUCTION

Dust formation in processing discharges is usually an unwanted process, because dust incorporation in deposited features leads to malfunctioning devices. As devices become smaller and smaller, the size of "killing" dust particles in micro-electronics in the near future reaches the 10 nm range. Particles, however, can also be beneficial. When nm sized particles are incorporated into the intrinsic layer of an amorphous silicon based solar cell, they enhance the stability against the Staebler - Wronski effect that reduces the cell efficiency under irradiation[1]. It is obvious that in order to control the flux of particles toward a substrate, one must understand the mechanisms behind their formation and their transport. With increasing importance of small particles, especially the transition from "large molecules" to "small particles" becomes important. This is the phase prior to the coagulation phase, in which particles cluster to form cauliflower shaped larger (10-20 nm) particles. This is the so-called \( \alpha - \gamma \) transition. It is characterized by a sudden drop in electron density and an increase in electron temperature[2, 3].

In astrophysics dust plays a role as the precursor for planet formation. In carbon rich star envelopes carbonaceous clusters are formed, presumably via chains of polycyclic aromatic hydrocarbons (PAH's), a mechanism also used to predict soot formation during
Discharges in hydrocarbon gases are used to study the generation of dust during carbon deposition. Partly these studies are also done in the context of astrophysics, but here again the role of negative and positive ions cannot be excluded, making the circumstances quite different from those expected in stellar atmospheres. Another difference with the astrophysical situation is that although discharges in general produce a flux of UV photons, photo-ionization and photo-detachment are not expected to be important, so their influence on the dust formation is not expected to be large, although a role during the coagulation phase cannot be excluded.

Dust formation in present day Tokamaks is mostly due to the ablation of wall material, already in the form of particles. Other mechanisms proposed are coagulation from oversaturated vapor and the ionic reaction chains also observed in processing discharges. In future devices, starting with ITER, the plasma in the divertor region is expected to be cold (≈ 1–5 eV) due to detached operation. A high particle (10^{24} \text{m}^{-2}\text{s}^{-1}) and energy flux (10 \text{MWm}^{-2}) enter this region. As the arriving fluxes are expected to be strongly modulated due to transport fluctuations in the boundary of the confined core plasma, strong evaporation may occur, promoting dust formation from oversaturated vapor that interacts with the hydrogen and hydrocarbon neutrals and ions already present.

Usually, the first steps in the chemistry of processing plasmas are reasonably well known and validated against experimental data. Particle formation starts from polymerization involving large ions or repeated insertion of certain groups in linear or cyclic molecules. Rate constants for these processes, however, are usually a sophisticated guess, assuming that properties will obey a certain scaling with the size of the molecule or ion. Little is known, however, regarding the transition from large molecules (typically ten atoms) to small particles containing hundreds of atoms. An important feature is the accumulation of small particles (typically 2 nm, or 100-200 atoms) prior to a fast coagulation phase. This coagulation can be described using techniques from aerosol physics. Since the charge distribution contains a fraction of positive charges, due to fluctuations, the coagulation is enhanced. The coagulation process thus strongly depends on the interaction of the particles with the surrounding plasma, because the particle charge is influenced by parameters like the ratio of the positive ion density and the electron density and the electron and ion energy distribution functions.

During the coagulation phase the particles are still so small that transport is fully governed by the electrostatic force and diffusion. Uncertainties in the description of the behavior are mostly due to incompleteness of probe theory and knowledge of the relevant plasma parameters. After coagulation, the particles are so large that they always have a negative charge and are confined by the sheath fields. Also in front of divertor plates in Tokamaks dust may be confined in a potential well. For larger particles, other forces become more and more important and lead to a spatial redistribution, that may even result in a dust free central void, caused by the ion drag force. For larger particles the growth is governed by deposition of neutral radicals and positive ions, similar to the growth of a deposited layer on a substrate. Eventually (on earth) gravity pulls the particles out of the discharge.

In this paper we will mainly discuss the phase prior to coagulation, where chemical processes are still dominant. Examples will be taken mostly from the silane-hydrogen plasma chemistry, indicating established knowledge and uncertainties.
carbon discharges show that there are similarities, but also clear differences with silane discharges. This will be discussed, focussing on needs for modelling these discharges. Also the conditions expected in the divertor plasma of ITER and devices beyond ITER will be discussed in relation to dust formation by A+M processes.

**SILANE-HYDROGEN PLASMAS**

**basic chemistry**

The basic chemistry in silane-hydrogen discharges is reasonably well understood [10, 11, 14]. Here we give only a short overview of the most important processes. The discharge is sustained by ionization of silane, producing various ions [14]:

\[ e + SiH_4 \rightarrow SiH^+_m + nH_2 + kH + 2e, \quad k + 2n = 4 - m \]  

and neutral radicals are generated by dissociation:

\[ e + SiH_4 \rightarrow SiH_m + nH_2 + kH + e, \quad k + 2n = 4 - m \]  

H atoms are also produced by dissociation of H\(_2\). The branching ratio for ionization of silane is known from experiments, for dissociation it is less well known. Estimates are based on photo-dissociation or on the branching for ionization. Agreement with experiments is fair, however, in the dust free regime. A sensitivity study showed that tuning the dissociation branching ratio was one of the ways to improve agreement with experimental data [10].

An important process for dust generation is the production of negative ions via dissociative attachment, where formation of SiH\(_3^-\) has the largest probability:

\[ e + SiH_4 \rightarrow SiH^-_m + nH_2 + kH, \quad k + 2n = 4 - m \]  

The neutral species react further, the most important processes being hydrogen abstraction from silane:

\[ H + SiH_4 \rightarrow SiH_3 + H_2 \]  

and insertion of SiH\(_2\) to form higher silanes:

\[ SiH_2 + SiH_4 \rightarrow Si_2H_6^* \quad Si_2H_6^* + M \rightarrow Si_2H_6 + M \]  

The excited disilane can also dissociate again into SiH\(_2\) + SiH\(_4\) or into Si\(_2\)H\(_4\) + H\(_2\). The disilane forms the basis for the formation of larger silane molecules, Si\(_n\)H\(_{2n+2}\) and their radicals, by further insertion of SiH\(_2\). These higher silane radicals may play a role in the deposition process when the residence time of the parent molecules is long enough [21]. The deposition process is described by means of reaction and sticking probabilities, yielding again fair agreement with experiments[10, 22].
The chain of processes leading to dust formation in silane is generally assumed to proceed via reactions between (vibrationally excited) silane and anions, as follows:

$$Si_nH_{2n+1} + SiH_4^{(s)} \rightarrow Si_{n+1}H_{2n+3} + H_2$$

$$Si_nH_{2n} + SiH_4^{(s)} \rightarrow Si_{n+1}H_{2n+2} + H_2$$

The internal energy stored in vibrationally excited silane is enough to overcome the barrier in endothermal reactions[23]. The dependence on the concentration of excited silane is one of the causes that make the process sensitive to the temperature of the gas, because the density of the excited molecules is determined by diffusion and quenching at the walls [3, 7, 24]. An influence of the gas temperature on the attachment rate could not be observed [25]. A role of radicals from higher silanes cannot be excluded. Reactions between large anions and large radicals may lead to small particles in a few steps[2].

Uncertainty in modelling arises from the unknown rate coefficients for the anion production and for the loss processes, like recombination with positive ions, electron detachment, and detachment by (excited) radicals. We have studied the influence of a number of assumptions using a 1-D model for a capacitively coupled RF discharge[10], including the chain of reactions with anions. The chain was stopped at anions containing 12 silicon atoms. This final stage thus also represents all larger anions[26].

Figure 1 shows the resulting density profiles of the anions for a discharge operated at a pressure of 40 Pa, a power of 5W power, using a frequency of 50 MHz, with a gas flow of 20 sccm of pure silane. The electrode separation is 3 cm. Clearly seen is the decrease of the density with increasing number of silane atoms. (Apart from the final accumulating stage, of course).

The rate coefficient for the anion reactions ($10^{-18}$ m$^3$ s$^{-1}$) is taken far below the theoretical maximum predicted by the Langevin rate ($10^{-15}$ m$^3$ s$^{-1}$), as suggested in[27]. Taking a large reaction rate results in the same density for all anions, which is not in agreement with experimental observations[2, 26]. Another path proposed to lead to large
FIGURE 2. The influence of reactions between SiH₃ and anions on the dust formation. The SiH₃ insertion has the Langevin rate, the rate for the standard SiH₄ insertion is varied. A large difference of the rate coefficients is needed to compensate the difference in densities. The same holds for the vibrationally excited SiH₄, where the larger rate coefficient stems from an Arrhenius factor[26].

anions is based on reactions with the SiH₃ radical[28]. Since the density of these radicals is at least three orders of magnitude lower than the SiH₄ density, the rate coefficients for radical reactions must be very high to make this path equally important. From our results we concluded that the radical path requires Langevin rates, in combination with our low estimate for the SiH₄ reactions[26]. Figure 2 shows the contribution of the SiH₃ path when it is assumed that the rate for the process is the Langevin rate, while the rate for the SiH₄ insertion is varied, confirming the statement above.

The steady state solution of the particle balance of the anions, including only silane insertion and recombination with positive ions, results in a simple decay of the densities:

\[
[Si_{n+1}H_{2n+3}^-] = [Si_nH_{2n+1}^-] \frac{[SiH_4]k_{r,n+1}}{[SiH_4]k_{n+1,n+2} + \sum [Si_lH_{m}^-]k_{rec,n+1}}
\]

(7)

Experimental data in [2] show a decay with a factor ≈0.8 for every step, indicating that the loss due to recombination (and other processes) is about 25% of the production rate. The reactions are fast, in experiments the large negative ions are present on a timescale of milliseconds. Obviously, when one continues a series like the one above, the density of very large ions must be very small. Experiments, however, show an accumulation of particles with a size of 1–2 nm, prior to the \( \alpha \rightarrow \gamma' \) transition. This implies that either the loss rate must decrease or the production rate must increase, or both. Possible mechanisms are reactions with larger silanes (SiₙH₂ₙ₊₂) or (large) silane radicals (SiₙHₘ). Indeed these species can reach high densities, as shown in figures 3 and 4. Little is known about the reaction rates[16], but assuming the same rate as for SiH₄, the parent molecules of the higher silanes can give the same contribution as silane itself. The electronegativity may change, also due to restructuring of the particles. The large negative ions in the observed mass spectra are hydrogen poor[2], and are no longer linear molecules but contain cross-linked silicon bonds. What holds for the SiH₃ insertion in
FIGURE 3. Density profiles of parent molecules of higher silanes in a silane discharge operated at 5W, 40 Pa, and 50 MHz

FIGURE 4. Density profiles of radicals in a silane discharge operated at 5W, 40 Pa, and 50 MHz

the anions of course also holds for the reactions with large radicals. The rate coefficients must be very high to compete with the SiH₄ or SiₙH₂ₙ₊₂ insertion. The density ratio that is to be compensated is even much larger.

Once the particles have reached a size of about 2 nm, the growth stops. The density increases up to more than 10¹⁶ m⁻³, after which a fast coagulation to larger particles (>10 nm) occurs. This process of accumulation and coagulation requires two seemingly contradictory conditions. The particles must have some negative charge, in order to be confined, but a negative charge would prevent coagulation. It is believed that the particles have a charge that is negative on average[16], but with fluctuations yielding even positive charges[17]. Like in aerosol physics, a high concentration then leads to a fast coagulation[7]. A feature that could help in confining the particles is the fact that
the charge of the particles is not uniform throughout the discharge[25]. In the presheath
the average electron energy is higher than in the centre, while the positive ions are
accelerated, resulting in a lower collection probability. This makes the particle charge
more negative. An example is shown in figure 5, where the charge on particles of various
sizes is plotted against the position in the discharge. The barrier is clearly visible.

Thus, once the coagulation phase sets in, it is no longer the lack of A+M data that
creates the uncertainty, but the interaction with the plasma in which the particles are
embedded.

HYDROCARBON PLASMAS

basic chemistry

As an example of the chemistry in hydrocarbon discharges, let us consider acetylene,
C\(_2\)H\(_2\). Other hydrocarbons also produce dust, but CH\(_4\), for instance, only when a suf-
ficient amount of C\(_2\)H\(_2\) has been created[5]. The C\(_2\)H\(_2\) chemistry has been modelled
for radio-frequency discharges, but not as extensively as the silane chemistry [12, 13].
An important feature is the strong C-C bond, that is present in most of the hydrocarbon
species that are generated and distinguishes acetylene from other hydrocarbons[5].
Ionization by electron impact produces C\(_2\)H\(_2^+\) ions that react further with acetylene to
produce larger ions:

\[
C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2; \quad C_{2n}H_2^+ + C_2H_2 \rightarrow C_{2n+2}H_2^+ + H_2 \quad (8)
\]

These positive ions are observed in mass spectra and peak at C\(_4\) or C\(_6\) containing
ions. Typical is the absence of ions with an uneven number of carbon atoms and the low
hydrogen content.
The neutrals that are generated show the same picture. Dissociation of acetylene produces the C₂H radical that is inserted into C₂H₂, to form C₄H₂ and atomic hydrogen. Larger radicals like C₂₃H can be formed by electron induced dissociation of C₂₃H₂. A variety of neutral-radical reactions thus leads to larger and larger neutral species. An analysis of ions and neutrals with up to 16 carbon atoms, using the Li⁺ attachment technique[29], shows this. The appearance of hydrocarbons with six C atoms and a larger number of H atoms seems to indicate the generation of aromatic rings, but this remains an open issue[5, 29]. Reactions including negative ions are not frequently included in the chemistry, although it is well known that the electron affinity of hydrocarbon radicals can be sufficiently large to produce stable anions. The primary ion in acetylene is C₂H−. It can be incorporated in neutral species to yield larger negative ions. These are observed in mass spectra of modulated discharges. The tendency of formation of aromatic rings seems also present in the negative ion spectrum[5]. In addition, infrared absorption spectroscopy also shows the presence of cyclic molecules[30].

**dust formation**

Mass spectra of positive and negative molecular ions show approximately the same features, indicating that more pathways towards dust formation exist in the chemistry. However, measurements over a larger range in masses showed that negative ions are again the most important dust precursors in processing discharges[31]. This is to be expected since positive ions are extracted from the discharge before they can grow further. Recombination between large positive and negative ions could lead to very large neutral species that can become negative again by electron attachment. Also reactions with or between unsaturated large linear and cyclic species could provide a pathway to dust. One should also realize that in the discharge a large amount of atomic hydrogen is present from the dissociation of H₂. This could play a role in the chemical activation of hydrocarbon species by hydrogen abstraction, similar to silane. Hydrogen bonds in hydrocarbons are stronger, however, and the opposite process, passivation, may be important as well, especially for large molecules, that can easily accomodate the energy involved.

In astrophysics the common route adopted for dust formation is the insertion of C₂ containing species in aromatic rings, forming larger and larger PAH’s[4]. The existence of this route is confirmed by experimental observations in processing reactors, where fullerene-like structures are found[32]. The formation of PAH’s has also been included in a model for acetylene RF discharges[15]. One of the results was that the formation of the first aromatic ring (benzene) strongly depends on the gas temperature.

Obviously, data are needed regarding the unsaturated PAH chemistry, electronegativity, etc., in order to understand the whole path from basic chemistry to small clusters.

The discussion above shows that the dust formation mechanisms in hydrocarbon discharges are far less understood than those in silane-hydrogen. Especially the role of PAH’s is not clear. It should be noted here that the discharge conditions also play a very important role. The PAH-route was first studied in relation to combustion, and applied to carbon rich stellar envelopes. These conditions are quite different from the low pressure
processing discharge, where stabilization of reaction products by collisions with a third body is less important and confining electric field prolong the lifetime of negative ions. In future Tokamaks, the PAH route will probably prevail again, as will be discussed below. To establish the importance of the various mechanisms extensive experiments are needed, in addition to A+M data.

**DUST FORMATION BY A+M PROCESSES IN TOKAMAKS**

While in present-day Tokamaks dust is mostly produces by flaking of redeposited carbon, this will probably change completely in the next generations, starting with ITER. In order to protect the divertor from the incoming high particle and heat load, reactor operation must be in a detached mode, where a low-temperature plasma is generated in the divertor chamber, for instance by gas puffing. The plasma will have a temperature in the eV range, suppressing physical sputtering, but enhancing chemical processes. The hydrogen plasma etches carbon from the wall, introducing a hydrocarbon flux into the divertor chamber. These hydrocarbons are ionized and redeposited. Particle fluxes will be very large, \(10^{24} \text{ m}^{-2} \text{s}^{-1}\), so each site of the surface will be hit every \(10^{-5} \text{ s}\). This may well lead to a large variety of heterogeneous reactions, that do not seem to play a role in processing plasmas. This is an open field, that will hopefully be covered by linear machines in the near future[33]. Another major difference with processing plasmas is the extreme heat flux. In ITER this will be \(10 \text{ MWm}^{-2}\) on average, but due to edge instabilities in the main plasma, much larger peak loads will occur. Especially during these peaks carbon will evaporate from the surface, producing an oversaturated vapor. This carbon is the basis for formation of polycyclic compounds, as has been shown in experiments with electron beams[34].

**REFERENCES**

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