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Plasma processing and the importance of surface molecule generation

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In plasma processing the efficient dissociation of molecules is the key element for producing the precursors for plasma deposition, surface modification, and molecule conversion. During these processes always molecules are generated, as e.g. H_2 in deposition of hydrogenated carbon or molecules may be converted to new molecules. Measurement of molecules is thus a possible way to investigate the reactive pathways in plasma chemistry. It appears that the surface plays a pertinent role in the formation of molecules. This became clear from the study of several plasmas, including the remote plasma of an expanding thermal plasma. Measurements by mass spectrometry and infrared absorption indicate several dominant pathways as re-formation of N_2 and O_2 besides a small percentage of NO in N/O, the formation of ammonia in N/H, of water in H/O and CO and H_2 in H/C/N/O containing plasmas. The presence of excited molecules presumably generated at the surface bordering the plasma indicates the presence of modified chemistry in a plasma environment.

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1. Introduction

Plasma processing has become an important new approach for deposition of thin layers advanced materials, for the modification of surfaces and for the conversion of molecules [1-5]. Plasma is used because of its ability to create high radical and ion fluxes. Thus new chemical pathways are opened: new materials can be exploited, and molecules can be converted to new molecules with possibly high selectivity. In plasma the first step is ionization, which is accompanied by dissociation. This leads to ion and radical fluxes, which are thus linked to the ion-electron production. If in the gas-phase radical reactions are absent, or do not lead to stable molecules then the produced flux arrives sooner or later at the surface [6]. There, the surface first becomes passivated; then additional radicals produce in a modified surface chemistry new molecules or lead to deposition.

These processes look similar to classical hot gas chemistry as in heterogeneous catalysis [7]. There is however a significant difference in the surface chemistry. In catalysis the absorption at the surface is slow and the reaction and desorption relatively fast. Hence a large number of surface sites are available for catalytic reactions. In plasma “catalysis” the radical adsorption is fast and with the large fluxes the surface becomes immediately saturated with radicals. What happens next is still not fully clear, but additional adsorption with smaller binding energies and subsequent fast chemistry is a possibility.

The plasma approach differs thus from thermal methods and offers further several advantages above more classical approaches, as CVD. The plasma can be changed in very short times and also fast change of surface temperature and conditions by pulsing of the power becomes possible.

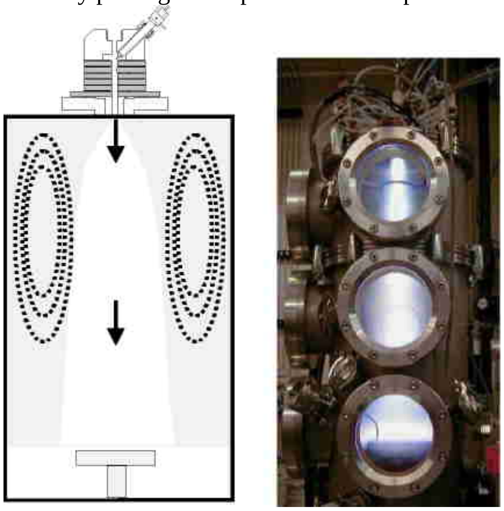

Fig. 1, Sketch (left) and photograph (right) of the expanding thermal plasma. From the cascaded arc source at the top, a plasma beam, surrounded by re-circulating flows, expands into the vacuum vessel.

These virtues have hardly been exploited as the very mechanism of the plasma process is still under considerable debate. It is for this reason that a study was undertaken to investigate the processes in plasma volume and at bordering surfaces. Commonly this is attempted by measuring radical densities or relative behavior. Then however only a small part of the chemistry can be observed as it is usually difficult to observe all the important radicals at the same time. As the produced radicals remain radicals until they participate in surface processes to form new (and possibly other) molecules, then another option is to monitor the generation of new molecules and the consumption of injected molecules. Thus in this work the chemistry was analyzed by measuring the *stable* molecules [8-9]: the ones consumed and the ones formed. This way it is also possible to obtain an insight what happens at the surface. Optimally this is done in conditions that all injected molecules are dissociated before being pumped away, so that each molecule participates in the reactions at least once in its lifetime. If that is not the case, the consumption of injected molecules is not complete and injected molecules remain being seen.

2. Remote plasma processing

The main sequence with plasma processing is thus the creation of plasma, the production of radicals, transport, and surface reactions. In the latter the actual process takes place, like deposition and surface modification. During these processes always molecules are generated, as e.g. H_2 in deposition and thus the process can be monitored by observation of produced and consumed molecules [8-9]. This somewhat global view of plasma dissociation and surface association has been the result of the search of fast plasma deposition and other processing methods. If the energy load at the surface limits the process rate, then a separation of plasma source and plasma deposition is advantageous. Hence the remote source approach, cf. fig 1, was introduced. The plasma production (with associated power load) is geometrically separated from the plasma process. In this case the ionizing plasma is upstream with downstream the recombining plasma. With the ETP method, (expanding thermal plasma [5-6]) an atomic plasma source, operated at high pressure, delivers a sonic expanding plasma. High velocities and low electron temperatures (equal to the heavy particle temperature, which is thus relatively high), characterize these plasmas. As the temperatures are in the sub-eV range electron induced ionization and dissociation is impossible [5-10]. Dissociation of downstream-injected molecules takes place mainly by charge transfer of molecules with the ions from the source and subsequent dissociative recombination of the resulting molecular ion [11-13]. For dissociation heavy particle initiated reactions have a strong advantage: they are not so dependent on energy distribution, they may be rather specific and they have usually large cross sections. For our purpose the dissociation can thus easily be estimated on basis of the measured source strength of Ar^+ ions or atomic radical (H) atoms.

The sequence of charge transfer and dissociative recombination offers thus an effective way of dissociation. It has also a downside: it will lead to a strong decrease of the ion and electron density downstream from the source, which by the way leads also to a strong production of atomic fragments. This plays a role in particular when hydrogen is admixed: the effect of H_2 molecules is so strong that in practice one has to choose to work either with Ar^+ ions or with H atoms as primary chemistry [5-6].

A second example of the heavy particle initiated dissociation forms the processes involved in deposition of amorphous carbon layers. Here the Ar^+ ions from the source are used to dissociate injected C_2H_2 molecules by charge transfer; dissociative recombination of the resulting $C_2H_2^+$ ions leads to mainly C_2H radicals. These radicals (possibly modified to higher hydrocarbon by polymerization reactions [13]) lead to deposition. During this process hydrogen molecules are produced, whereas carbon remains in the growing layer at the surface. If CH_4 is injected a significant amount of C_2H_2 is produced and thus molecule formation at the surface accompanies the deposition [14].

Alternatively H atoms from the source can be used; an example of this route forms deposition of a-Si:H layers with the use of SiH_3 radicals produced by H-abstraction of SiH_4 [15]. In this reaction and in deposition H_2 (and SiH_4) are produced; thus also in this example new molecules are produced.

So one aspect, which accompanies deposition, etching, surface modification and other plasma surface interactions, is the production of (new) molecules and measuring these new molecules can be used to investigate the chemistry in volume and at the surface of molecular plasmas.

In a plasma environment the process at the surface is different from the usual one in chemistry, CVD and catalysis. The difference lies in the relatively high flux of radicals, commonly in the order of 1000 monolayers/s. Thus at the usually low surface temperature full coverage results and probably additionally adsorbed hot atoms start to play a role in the chemistry [6, 8-9, 16, 17, 20]. To investigate these mechanisms, studies have been performed on the generation of molecules, as the formation of NO, of ammonia, and of water in N/O/H mixtures, i.e. for non-depositing systems. This is performed in different plasmas at two universities, at pressures around 10- 100 Pa.

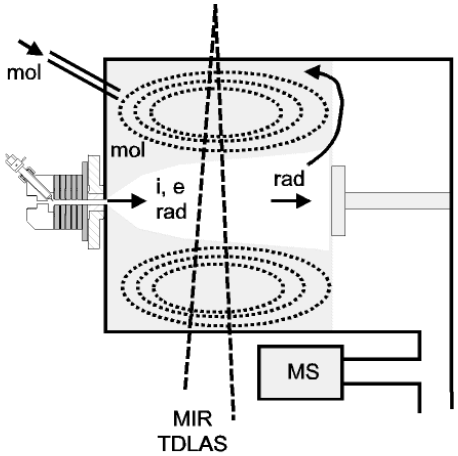

Fig. 2. Sketch of setup with diagnostics. Ions (i) and electrons (e) leave the source, interact with injected molecules (mol) and produce radicals (rad).

3. Molecule formation by surface association in plasmas

In the low temperature recombining plasma expanding from the source, charge transfer and dissociative recombination form the radicals. These are then transported by convection and diffusion to the surface during the re-circulation in the outer region of the plasma, fig 2. At the surface they may be adsorbed, but also be reflected; in the latter case the density builds up until the *net* flux is equal to the production of radicals. Thus the lower the surface association coefficient, the higher is the radical density. In pure gases like N_2 (or H_2 or O_2) the γ coefficient influences only the N density, not the final association to molecular N_2 at the surface. However, this is not anymore true for mixtures. If e.g. O_2 is added to nitrogen, the nitrogen atoms can also be consumed in the gas phase in reactions as $N + O_2 \rightarrow NO + O$ and $N + NO \rightarrow N_2 + O$. It is clear that in that case the combination of surface accommodation coefficient and of volume reactions determines the result in terms of molecular abundances [17-21]. In fig 2 a sketch is given of the expanding plasma and circulating plasma at the outside [17]. Also the two diagnostics used are indicated: mass spectrometry and diode laser absorption. Typically one uses plasma flows of 50 scc/s (1 scc/s = 2.5×10^{19} /s). In argon 10% is ionized. The residence time, determined by the pumping speed is typically 0.1 s. As a first example the formation of NO molecules, measured with mass spectrometry and with diode laser absorption, is shown in fig 3 [9, 17]. The result is that 3-5 % of the injected N_2 and O_2 are converted to NO, a result found earlier for many types of plasma [4, 19]. Chemkin simulations [20] show that, even though here the two volume reactions mentioned above are active, still surface association with the O atoms, resulting from these reactions is the dominant mechanism. This result points to a dominant production of N_2 and O_2, which should be expected on the basis of chemical bonding. However, that a substantial amount of NO is produced indicates that a physical aspect plays a role [8, 9, 16].

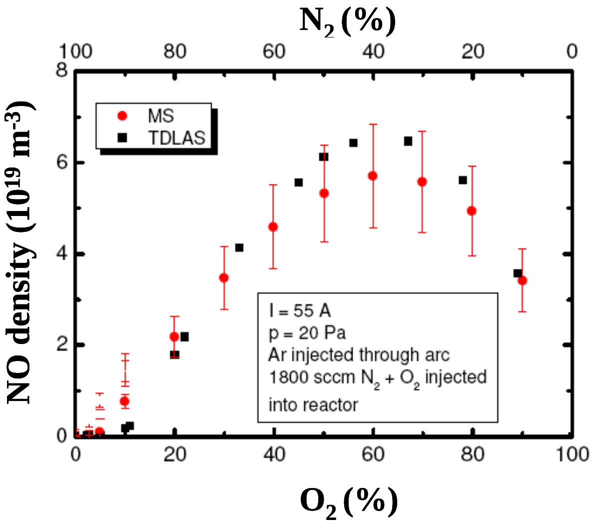

Fig. 3. the NO density as function of the admixed fraction O_2, with respect to the total injected flow of N_2 and O_2. The total flow of N_2 and O_2 is kept constant [17].

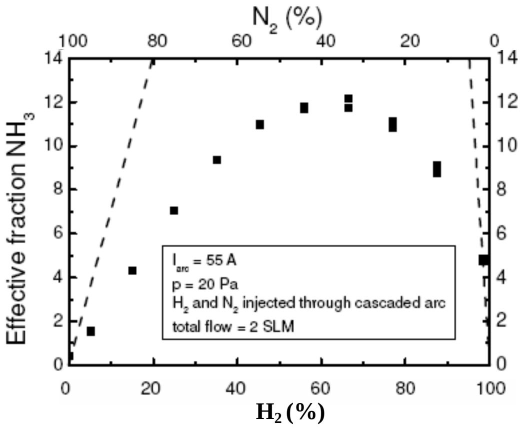

Fig. 4. Mole fraction of NH_3, normalized to the injected flow of $N_2 + H_2$, as a function of the admixed fraction of H_2 [21]. The dashed lines represent the maximum effective fraction of NH_3 that can be observed, when all the H_2 (right) or all N_2 (left) is converted into NH_3 .

Also the formation of ammonia in a N_2/H_2 plasma was studied. The result is shown in fig 4 [21], in which the ammonia is given as fraction of injected N_2/H_2 gases. A maximum NH_3 fraction above 10 % is reached. At low fractions of injected N atoms practically all these minority atoms are used for NH_3 formation. This can only be explained by a sequence of pick up reactions at the surface, forming with the N atom arriving, NH, NH_2 and finally NH_3, which desorbs. Unlike the NO case here there are no competing volume reactions. A third example forms the changes imposed by the addition of O_2 to the N_2/H_2 system. From fig 5 it is clear that a little amount of oxygen directly kills the NH_3 production. Later it appeared that water is formed instead, see e.g. fig 6 [8, 20]. This fits perfectly the picture of molecule formation by picking up adsorbed fragments as NH_2 or OH at the surface.

This chemical system has also been tested [8] in another experiment, the planar microwave discharge in the INP institute in Greifswald [22, 23]. These experiments have shown a good correspondence to the recombining ETP plasma at the TU/e in Eindhoven [8, 20]. It suggests that under the high load of radical fluxes the surfaces become saturated and the specific nature of the surface becomes less important.

At this point it is relevant to memorize the various surface processes as Langmuir Hinshelwood (LH) and Eley-Rideal (ER), respectively reactions between adsorbed fragments and direct pick up [6]. In the plasma case, the surface is fully saturated and LH desorption is too slow. It is possible that in that case the chemistry proceeds via hot mobile precursors, less bound to the surface, like, H, N, O, NH, NH_2, NO, OH.

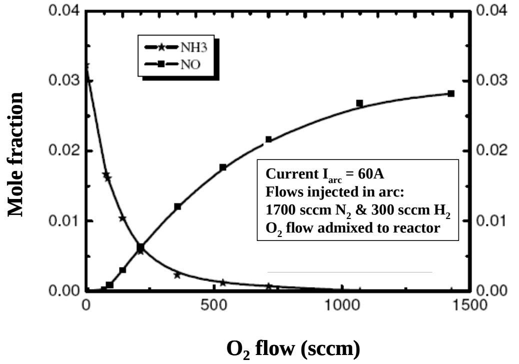

Fig. 5. Decrease in the mole fraction of NH_3 and simultaneous increase in the mole fraction of NO, when O_2 is admixed [19].

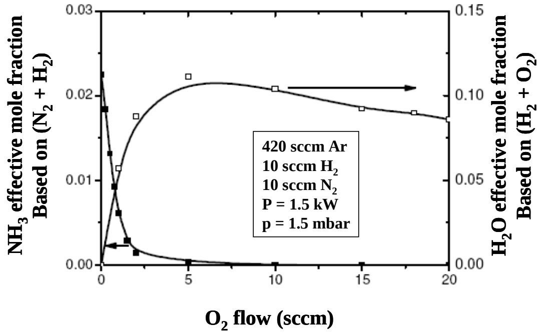

Fig. 6. The effective fraction of NH_3 and H_2O in a microwave discharge as function of admixed O_2 flow [8]. Note the differences in scale for NH_3 (left) and for H (right).

The change from an unoccupied surface to a fully covered surface has been addressed in an experiment [24] in which the time dependence of the surface γ and radical loss was obtained. In a low pressure helicon discharge in oxygen, the pulse length of discharges was varied, from very short to long enough to produce a number of monolayers O atoms at the bordering surface. So for short pulses the O atoms arrived at an empty surface; for long pulses at a covered surface. The oxygen radical density during the pulse was measured as well as the decay time constant after the pulse. It appears that for short pulse times, when the surface was not fully covered yet, the O density was low and the time constant short. But with a sufficiently longer pulse, the O density increased as did the time constant. This clearly indicated the difference between an empty and a fully covered surface: at an empty surface γ was 1, the O atom density low; but once a monolayer is formed, γ decreased to around 0.1, the O density builds up and the decay time constant increases too.

Besides the experiments in expanding plasmas also experiments were performed in a microwave reactor in Greifswald. In fig 6 the variations of NH_3 and H_2O with increasing O_2 flux in N_2, H_2 plasma are shown, expressed in effective molar fractions (measured mole fractions multiplied by the total injected flow, divided by the flows of either N_2+H_2 or N_2+O_2, thus excluding the inert carrier gas Ar) [25]. It is evident that the behavior is very similar. So, in a plasma without oxygen NH_n radicals get the time to build up until NH_3 is formed [25]. In the presence of oxygen the OH radical becomes the dominant radical and thus water is formed. The experiments in Greifswald show, as those at the TU/e, that the NO formation, which is similar in reduced molar fraction, is hardly affected by the presence of H_2.

Further work at the INP in Greifswald has been undertaken to include measurements with mass spectroscopy. Also C containing gas (CH_4) was admixed and thus a full view on H/N/O/C mixtures was obtained. It appeared that some gases were formed dominantly whereas others appeared only in smaller fractions. Dominantly always CO, H_2 and N_2 were formed, followed by O_2 and H_2O. Smaller levels were found for NO, NH_3 (if O poor), HCN, and hydrocarbons [8], fig 7. Again it appears that molecule production follows several rough laws quite independent of plasma type and material walls. Molecule formation appears to be controlled by association of atomic and molecular radicals residing at the surface. The question arises if this mechanism offers new possibilities to produce new molecules under controlled conditions.

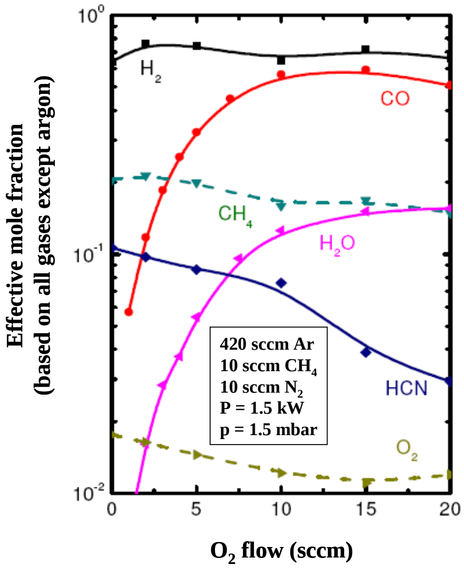

Fig. 7. Most abundant molecules besides Ar, in the microwave discharge, fed with a mixture of CH_4 and N_2 in argon and a varying amount of O_2. Flow settings Ar/CH_4/N_2 = 420/10/10 sccm, p = 1.5 mbar, P = 1.5 kW [8].

4. Formation of *excited* molecules by surface association in plasmas

It has been suggested that radicals, which associate to new molecules at the surface, are of "hot" type with limited bonding energy to the saturated surface. Then molecules can be formed with a substantial internal energy and in this section some evidence of these excited molecules is shown.

First in the expanding plasma emanating from a hydrogen source, substantial amounts of ro-vibrationally excited hydrogen molecules have been observed by CARS [27] and by VUV-LIF [28]. It appears that a large overpopulation exists for J levels with energy spacing above thermal energy with apparent temperatures higher than 4000 K.

Also vibration is non-thermal with similar apparent temperatures. The origin of these $H_2(r,v)$ molecules is suspected to be at the surface of the exit nozzle of the arc source [29], where very high fluxes of H atoms are present. The presence of ro-vibrationally excited $H_2(r,v)$ is important in the sense that reactions become possible, which are very unlikely for ground state H_2. First the presence of $H_2(r,v)$ promotes the conversion of H^+ to H_2^+ ions by charge transfer. The latter ions recombine dissociatively into H in the n=3 state thus emitting Balmer α. An important reaction is the formation of negative H^- ions by dissociative attachment. On its turn these H^- ions can recombine by mutual recombination and leave one of the two atoms in a high excited state and blue Balmer emission [30].

A second example of such excited state emission is observed in a nitrogen discharge. At high fluxes close to the surface additional emission is present, apparently induced by excited particles coming from the surface. The emission consists of the first positive system of $N_2(B\rightarrow A)$ and the first negative system of $N_2^+(B\rightarrow X)$. Both emissions cannot be excited by electrons as T_e is around 0.1 eV and thus the only possibility is release of excited N_2^* molecules from the surface [31].

A third example is the emission of orange light when both nitrogen and oxygen radicals approach a surface [16, 32]. This semi continuum, attributed to NO_2^* resembles the shuttle glow, emitted at the front of a shuttle re-entering the earth atmosphere [33].

5. Conclusions and further prospects

Molecule formation in plasma chemistry occurs to a large extend by dissociation in the plasma and by surface association of produced radicals. In this way the, in heterogeneous chemistry difficult, dissociation at the surface is circumvented. In plasma the fluxes to the surface are also commonly much larger than classical LH desorption and thus the surface is fully covered with radicals and passivated. It is thus to be expected that generation of molecules is different. These processes can be followed by observing the use of injected and the generation of new molecules in the plasma. In particular non-depositing systems containing N/ H/ O have been studied. In N and O plasmas mainly N_2 and O_2 are formed, but also a few percent NO is produced. It appears that NO is dominantly formed at the surface, but that the final density is determined by N atom induced volume processes. This forms also the explanation for the conversion rate of a few %, which is observed also elsewhere. The production of NH_3 in N-H plasmas is observed to be quite effective. It proceeds by association of H atoms to N, NH, NH_2 radicals at the surface. If O is added to the N/H mixture the NH_3 production is decreased and H_2O is formed instead. This can easily be understood as the formation of OH radicals at the surface replaces NH_2 at the surface if oxygen is added. Molecules are formed by association at the surface: by reactions with surface adsorbed fragments, like OH and H leading to H_2O and H and NH_2 forming NH_3. If carbon is added to an oxygen containing plasma first CO is formed [8]. Only after consumption of the available O or C hydrocarbons (for small O) or water and oxygen (for small C) are formed.

The results indicate that possibly surface processes depend on the rate of arrival of radicals. Thus optimization of flux production at minimized gas flow and power will open the plasma regimes even more. It suggests also, that designing properly the surface area and surface to accommodate the radical flux optimally is a subject worth investigating in the future. As the surface is passivated it is to be expected that the surface material will have a smaller influence and thus other less specific materials may be used. Then an aspect not exploited enough is the possibility to use the time domain. Plasma can be modulated on time scales of milliseconds and thus on conversion on monolayer amounts. If specificity can be achieved then fast changeable specific generators become into sight. It forms a new line of possible detailed chemistry.

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