Plasma Processing and Chemistry

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Abstract. The growing field of applications of plasma as deposition, etching, surface modification and chemical conversion has stimulated a renewed interest in plasma science in the atomic physical chemistry regime. The necessity to optimize the various plasma processing techniques in terms of rates, and material properties has made it mandatory to take a new look at the various processes, as fragmentation, plasma and radical transport and plasma surface interaction with advanced diagnostics and with modellization. Many types of plasmas are used in the technology of plasma chemistry: varying from RF—glow, discharges, coronas to high density arcs. The physics involved will be illustrated at the hand of important examples: etching and modification of surfaces and the deposition of thin layers of amorphous (a-C:H, a-Si:H) and crystalline (diamond, graphite) layers. Besides dissociation and ionization in the plasma, wall association, recirculation, cluster formation and energy flows are important issues. These conclusions are also pertinent to the new field of waste destruction and are directly relevant to the economics of the plasma process.

1. Introduction

Plasma processing, deposition and etching, modification, conversion and nucleation in or with plasmas has become important in practically all aspects of high technology and more traditional industries [1-4]. The economic interest in plasma processing for microelectronics, sensors, solar cells, hard coatings is enormous and is in the order of tens of billions of dollars [3]. The development of the field has first been phenomenologically; at present it develops into a new professional sub-discipline, with systematic analysis and modellization in connection with material science, vacuum science and gaseous electronics. The effectivity of the plasma as chemical medium is a consequence of the high reactivity related to the presence of electrons, ions, radicals and other active species. Both electron and heavy particle kinetics play a role in transferring kinetic energy to internal energy. The high energy density of the plasma medium makes it possible to obtain large radical fluxes which carry a high energy flow at low densities. The virtue of plasmas lies further in the nearly unlimited possibilities for atomic combinations. Practically everything is possible: deposition of crystalline or amorphous thin layers, etching, surface modification, chemical conversion,
synthesis and destruction, cluster formation and production of powders. The low inventory in the conversion process makes plasma processing inherently relatively clean and safe and is environmentally friendly if properly designed. The only but important limitation of plasma processing is the relatively high price; also this aspect is linked with the two earlier mentioned factors: high energy density and small material inventory (and thus throughput). It is for this reason that more systematic scientific support is desired, like that traditionally present in the plasma fusion community.

![Diagram](image)

**Figure 1.** Plasmas characterized in terms of electron density and ionization degree for several plasma applications and plasma types; gd: glow discharge, µd: microwave discharge, s: surfatron, ag: anomalous glow, rfi: rf induction plasma, h: helicon discharge, ecc: electron cyclotron resonance discharge, icp: inductively coupled plasma, epb: expanding plasma beam, va: vacuum arc, t: thermal plasma, hca: hollow cathode arc. At the bottom the required power density is indicated. Adapted from [5].

Important applications of plasma processing are to be found in Integrated Circuit (IC) semiconductor electronic industry, polymer films, optical layers, protective
layers, membranes, biocompatible layers, corrosion- and wear resistant coatings, production of ceramics (including high T superconductors) and catalysts, conversion and destruction of chemical compounds and waste, plasma spraying, and recovery of materials from metal scrap. Plasma processing ranges from high added value processes as in IC fabrication, intermediate cost processes as large area thin films for solar cells, to low added value processes as destruction of waste materials, and in the metallurgical industry. In the first class the cost of the process is less important and the quality of the layer is the key issue. In the intermediate class of processes (as thin layer solar cell fabrication) acceptable cost figures could be $10-100/m^2 for a 1 \mu m$ thin layer, which is equivalent to $10-100/g$. In the low added value processes prices of $1-10/kg have to be reached to become economically feasible. In most cases the time duration of the process and associated depreciation cost determines the price and high power, large throughputs and high energy and material efficiencies are essential. This line, from high added value processes to the processing of larger volumes (cf. also fig. 1, [5]) will be our guideline in the description of plasma processing.

2. Plasma processing, a short summary of etching and deposition mechanisms

In the IC process industry (and in e.g. solar cell fabrication) RF excitation is the traditional technology. We will first describe the dry etching of patterned wafers, which is a crucial plasma assisted step in IC-(sub)micron technology. The process, e.g. fluorine etching of SiO$_2$ is relatively well understood because of detailed beam studies [6], many diagnostics studies [7] and modelisation including wall processes [8]. Between two parallel plates of the size of a wafer an RF field is applied with typical conditions; pressure 10–100 Pa, 10–100 W RF power at 13.56 MHz with RF field amplitude and self bias of 100 V–200 V. Plasma etching can be performed
(e.g. SiO$_2$ by CF$_4$) with chemical selectivity (large etch rates for the material to be etched, e.g. SiO$_2$ and small for the photoresist mask) and anisotropy (i.e. fast etching in depth and slow lateral etching) as important figures of merit. In this way anisotropic etching will ideally lead to features of (sub) $\mu$m dimensions (fig. 2). The anisotropy and chemical selectivity are thought to arise because of the ion induced character of the etching by radicals. In this picture radicals adsorbed at the surface are stimulated to etch the surface by an incident ion. The side wall etching is inhibited because of the absence of ion irradiation and the protection by an inert (e.g. CF$_2$) inhibition layer (fig. 2). The etch rates are limited by the ion flux, which in turn is limited by the ionization production.

Plasma chemistry processes can all be characterized by five steps:
1. plasma production, electrons and ions serve as source for:
2. production of radicals by dissociation of injected and recirculating monomers in electron and heavy particle processes
3. transport of radicals and ions by diffusion or convection (typical transport times $10^{-4}$--$10^{-3}$ s)
4. surface interaction, adsorption, reactions, polymerization and desorption
5. recirculation of stable monomers and radicals, which add to the injected monomers (residence time 0.1--1 s).

Electrons heated in the RF-field ionize and dissociate the etchant gas: $\text{CF}_4 + e^- \rightarrow \text{CF}^+_4 + F + 2 e^-$ and $\text{CF}_4 + e^- \rightarrow \text{CF}^- + (4-n) F + e^-$. Ambipolar diffusion drives ions and electrons to the substrate, with ambipolar diffusion velocities in the order of the ion acoustic speed. Large bias potentials, in the order of the large RF field amplitude (100--200 V) accelerate the ions to the substrate. Radicals diffuse collisionally to the substrate where they may reflect, adsorb or react. Desorption of radicals (F, CF$_3$) contributes to the radical density and desorption of stable monomers (CF$_4$, C$_2$F$_6$) and etching products alters the gas composition, cf. fig. 3.

As dissociation is more effective than ionization the net flux of radicals (incoming -- desorbed) is somewhat higher than the ion flux (typically a factor 3--10). The incident radical flux is much higher because of radical density built up in the recycling. In the SiO$_2$ -- CF$_4$ case the etch rate is ion flux limited and can be estimated from a global inspection of the mass and energy balances [9], i.e. the existence demands of the plasma non equilibrium system. The mass balance equates the volume ion production to the ambipolar ion flux to the substrate:

$$\int \int \int n_{e_{\text{CF}^+_4}} k^{\text{ion}}(\hat{T}_e^{\text{eff}}) \ d \text{Vol} = \int \int D_{\text{amb}} \nabla n_e \cdot dS = \int \int \text{ion flux} \cdot dS$$
With typical values for the electron density \( n_e \sim 10^{18}/m^3 \), neutral density \( n \sim 10^{21}/m^3 \), ionization rate \( k_{\text{ion}}(T_{\text{eff}}) \sim 10^{-16} \text{ m}^3/\text{s} \) and distance between the electrodes (2 cm), ion fluxes of \( 10^{19}/\text{sm}^2 \) result. The mass balance determines for given dimensions and pressure (30 Pa) the effective ionization temperature, \( T_{\text{eff}} \sim 3 \text{ eV} \), which can be associated to the non-Maxwellian electron energy distribution function. This conclusion is independent of the value of the electron density as both the production and the flux are linear in \( n_e \). The mass balance learns that \( T_{\text{eff}} \) has to be large enough to guarantee sufficient production by ionization to balance the diffusive losses.

The electron density is determined by the energy balance; the dissipation results mainly from ion production and ion acceleration in the sheath and vibrational excitation of the molecular gas. Hence in the most simple form the Joule dissipation is equal to the energy carried with the ion flux and the (electron induced) vibrational heating of the molecular gas. As both losses are proportional to the electron density the allowable power density \( 10^6 \text{ W/m}^2 \) and energy flux \( (10^4 \text{ W/m}^2) \) limit the electron density to the quoted values at the 13.56 MHz excitation frequency. Hence the mass and energy balance determine the ion flux and thus the etch rate (or deposition rate). In the quoted example it is \( 10^{18}/\text{m}^2\text{s} \) equivalent to 1 monolayer per second and etch rates in the order of 1 nm/s result.

From this simple picture it is already clear that low pressure and high power favours ion induced anisotropy whereas chemical selectivity is optimum in a more radical rich situation at higher pressures and smaller power. At higher frequencies the density increases somewhat and self bias decreases; thus higher rates can be achieved and ion induced damage (but also the anisotropy) decrease.

RF excitation is also used for plasma deposition of thin layers of many materials, as polymers [2], diamondlike amorphous carbon, TiN, passivation layers and diffusion barriers. A pertinent example is the deposition of amorphous hydrogenated silicon, \( \alpha-\text{Si:H} \) for solar cells applications [4]. Silane (\( \text{SiH}_4 \)) admixed with \( \text{H}_2 \) is dissociated (\( \text{SiH}_n \)) and ionized (\( \text{SiH}_8^+ \)) see fig. 4. Is has been shown with infrared laser absorption spectroscopy (\( \text{SiH}_n \)), visible light laser absorption and laser induced fluorescence (\( \text{SiH} \)) [10] that \( \text{SiH}_3 \) is the most abundant radical, typically 10% of the parent gas. Detailed modelling with over 100 reactions has confirmed this finding. Hydrogen atoms may also participate in the radicalisation, either in the gas phase or at the wall:

\[
\begin{align*}
\text{H} + \text{SiH}_4 &\rightarrow \text{SiH}_3 + \text{H}_2; \\
\text{SiH}_4 + \text{H}(&\text{wall}) &\rightarrow \text{SiH}_3 + \text{H}_2
\end{align*}
\]

The deposition mechanism is commonly thought to be radical controlled [11],

![Figure 4. Densities of Si, SiH, SiH2 (measured by LIF and Intra cavity laser absorption) in a SiH4 plasma diluted by Ar (a) or H2 (b) at a total pressure of 0.3 Torr, a total flow of 10 sccm and RF power of 15 W; from Tachibana et al. [10].](image-url)
though other possibilities are mentioned [9], [12]. There is an influence of doping, which is different from SiH₄ feed than for SiF₄ [11]. Still many authors argue that SiH₃ is the preferred precursor as the mobility of this fragment at the surface is high, but also SiH₂ is mentioned [13]. Similar standpoint exist concerning the preference for CH₃ in diamond deposition but also here controversies exist. However it could also be that not so much the volume abundances of a specific radical is the determining factor, but rather the composition of the adsorbed layer. Of course the latter depends on the irradiation of radicals and thus the flux composition (at least the stoichiometry in Si/H) but also on energy irradiation, substrate temperature and thus the effective temperature of the adsorbed layer. The fact that many plasma methods lead to similar deposited material favours this more general point of view. Hence energy irradiation in the absorbed layer is of importance too and needs to be considered.

For deposition higher frequencies may be beneficial as in that case lower ion energies and higher rates are desired. Improvement of rate and quality of the layer have been realised this way for deposition of amorphous silicon for e.g. solar cell applications [14].

As has been stated, the rates of in situ processing are limited by restraints set by the plasma mass— and energy balances, or in other words, the existence demands. To circumvent these rate limitations by the existence demands other approaches have been pursued. They all have in common that plasma production is separated geometrically from the plasma treatment. This approach is commonly referred to as the remote plasma (source) treatment. In this way both production and treatment can be optimized separately. In these remote sources dissipated power can be chosen to be substantially larger (1kW) and the fluxes and thus the rates are consequently larger too. In e.g. electron cyclotron resonance sources (ECR) the plasma is produced upstream in e.c.r. zone (f = 2.45 GHz, Bres = 0.0875 Tesla) [15].

The resonance is not very critical as the plasma frequency is close to the electron cyclotron frequency. The energy density gradient and the diverging magnetic field lead to a fast flow of radicals, ions and electrons to the substrate. The final ion energy is coupled to the ambipolar acceleration process in the diverging field (and can be RF-bias enhanced) and is typically 20–200 V. These sources and related ones as helicon sources [16] operate at higher electron temperature and lower pressure. The newest type in this approach is the RFI (inductive) source, sometimes combined with minimum B magnetic confinement at sideways and upstream sides. This type of source relies on inductive dissipation and again the power density gradient and thus plasma energy density gradient leads to efficient transport of the produced ions and radicals from the upstream side to the downstream plasma treatment. For larger area deposition also non–resonant microwave excitation is used. The radiation leaks through vacuum sealed antenna slit and excites a homogeneous plasma, with again downstream deposition. A still other type of source is the surface wave heated surfatron [17].

An extreme form of separation of plasma production and treatment is found in the expanding plasma beam deposition (EPBD) method [18]. In this method the plasma is produced in a thermal arc close to atmospheric pressure and is expanded in a low pressure background where deposition, etching or surface modification occurs. Plasma production at high pressure — and thus high electron density — is very efficient and large ion flows can be achieved. In the expansion process (supersonic expansion, shock and subsonic expansion) the plasma cools from the 1 eV temperature in the arc to .3 eV in the treatment chamber. Hence the electron temperature is relatively low and the heavy particle temperature is relatively high (both .3 eV). In this situation the governing radicalisation kinetics are charge exchange and dissociative recombination, rather than electron kinetics as in the previous examples. For an argon arc and injected SiH₄ the following reactions may occur [19]:

\[
\begin{align*}
\text{SiH}_4 & \rightarrow \text{SiH}_2 + \text{H}_2 \\
\text{SiH}_2 & \rightarrow \text{SiH} + \text{H} \\
\text{Si} & \rightarrow \text{Si} + \text{e}^-
\end{align*}
\]
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\[ \text{Ar}^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{Ar} \]
\[ \text{SiH}_3 + \text{e}^- \rightarrow \text{Si}^+ + \text{H}_2 \text{ or SiH}_2^+ + \text{H} \]
\[ \text{SiH} + \text{Ar}^+ \rightarrow \text{Si}^+ + \text{H} \]

The example shows that very efficient transfer of the chemical energy to the formation of SiH radicals and even Si ions may result. There is no dependence on electron energy distribution functions and strong radicalisation to even atomic ions is possible. The charge transfer rates are typically \(10^{-15} \text{ m}^3/\text{s}\) and may depend on the ro(tational)–vibrational excitation of the parent molecules. The dissociative recombination reactions have rates of \(10^{-13} \text{ m}^3/\text{s}\) also probably dependent on ro–vibrational excitation. Similar reactions are possible with metastable argon atoms; however in most cases the ion density is larger than the metastable density even in recombining plasmas and charge transfer fragmentation dominates.

These examples show the 5 steps to be distinguished in plasma chemistry processes:
1. plasma production by ionization
2. production of radicals by dissociation of injected and recirculating monomers
3. transport of radicals and ions
4. surface processes as deposition and desorption
5. recirculation of stable monomers and radicals.

3. Surface modification and deposition by the expanding plasma beam deposition (EPBD)–technique

3a. Hydrogen treatment of surfaces

Restoration of archaeological artefacts by hydrogen atom irradiation [20] may serve as an example of surface treatment processes. Other examples are etching (with F or O) [21] nitriding [22] (with N) etc.. Here the plasma serves as a dissociator; for an argon/hydrogen arc charge transfer and dissociative recombination add to the electron dissociation in the arc. Again the chemical energy is stored in ions, but even more in atoms. For hydrogen arcs the radical (H)
flow may be as large as $1-3 \times 10^{21} \text{ p/s}$ which carry $\frac{1}{2}$ dissociation energy. In expansion in 1 mbar background typical plasma beam diameters range from 3 cm at the shock to 10 cm further downstream. Thus very large fluxes in excess of $10^{25}$ cm$^{-2}$ are reachable. Archaeological artefacts have been treated in this particle beam during typically 30 minutes. In particular those specimens which were post treated in a nitrogen plasma and further preserved by epoxy–sealing have shown very good results. By nuclear techniques the residual O and Cl surface abundances have been analysed. The results are shown in fig. 5 [23] in which heat treatments and plasma treatments are shown indicating that the presence of hydrogen and an elevated substrate temperature give nearly full chlorine reduction.

Hydrogen plasmas may serve as the most simple plasma chemical systems. Still two major complications become evident already from observation of the above mentioned plasma cleaning.

Figure 6a. Radial ion–density profiles for Ar and Ar–H$_2$ mixtures. The arc current is 45 A, the flow 3 slm and reactor pressure is 0.5 mbar.

Figure 6b. Variation of dissociation degree with flow in full H$_2$ at constant pressure (1 Torr) and arc current 35 A. From De Graaf et al. [23], [24].
The first one is an anomalously high recombination rate of hydrogen (containing) plasmas as compared to only weakly recombing argon plasmas [24]. This anomalously high recombination is due to the earlier mentioned charge exchange (\(H^+, Ar^+ + H_2^+ \rightarrow H_2^+ + H, Ar\)) and dissociative recombination sequence. Hence even atomic plasmas recombine because of the presence of residual molecules. Similar effects, though less severe are observed in other molecular plasmas, as e.g. in nitrogen [25] and methane seeded plasmas. Hence, molecules (essential in plasma chemistry) influence the ionization degree of higher density plasmas. The second point of interest is the very presence of the \(H_2\) molecules in the example. One major source is wall association of the primary H-atoms of the source with wall absorbed H-atoms. As practically always the residence time of particles in the machine is much longer than the circulation time these wall associated molecules are more abundant than the primary atoms. This is clear from fig. 6 in which the source dissociation degree and that in the expansion volume are displayed as function of flow at constant pressure and source current. It is clear that the \(H/H_2\) abundances are primarily influenced by wall associated molecules. Similarly if \(SiH_4\) would be injected in an argon/hydrogen plasma beam the \(SiH_4\) concentration (and wall associated disilane (\(Si_2H_6\) and \(H_2\))) will be determined by wall association and recirculation of molecules, rather than by the primary gas feed. Hence wall (and wall conditions) have a major influence on the molecular plasma constituents and therewith on the deposition process.

3b. Plasma deposition of amorphous and crystalline layers

Plasma deposition is a very wide area, with many material combinations and executed with many kinds of plasmas. Polymer layers from all kind of organic precursors, metal–organic layers – nitrides, – oxides with organo metallic gases or high vapour pressure fluids [2], semiconducting layers as a–Si:H and a–Ge:H [26] and hard protective layers as a–C–H, or diamondlike layers [27]. The most important issue here is an understanding of the deposition process, in order to obtain control on composition, morphology, (semi)conducting optical and electrical properties and (in particular for the intermediate added value processes) sufficiently fast rates.

Deposition of amorphous hydrogenated carbon [27] and – silicon [26] has been extensively investigated in view of application as protective coatings and in solar cells respectively. With elaborate diagnostic techniques radicals (\(SiH, SiH_2, SiH_3\) have been measured [10]; they all point to a dominance of \(SiH_3\) (similarly \(CH_3\) in the case of \(CH_4\)). This has been verified by extensive modelling [28] and there is more or less consensus on the preferred role of \(SiH_3\) and \(CH_3\) as precursors. But still the picture is far from clear and further clarification would facilitate the achievement of further advanced layers with new properties. Here we will summarize the results for amorphous carbon obtained with the fast expanding plasma beam technique [29]. In this method, quite similar to the H–atom source (fig. 6c), a very large radical flow is obtained by seeding of monomers as \(C_2H_2\) or \(C_2H_8\) (toluene) in the highly ionized argon plasma beam, which expands from a high pressure thermal arc source. As explained earlier the fragmentation is in this case mainly through heavy particle kinetics and radicalisation to \(C^+\) ions is possible. The growth rate measured by in situ ellipsometry increases linearly with monomer flow rate and values in excess of 100 nm/s over areas of 100 cm² have been reached. Layer properties as index of refraction, bandgap, hydrogen/carbon ratio and bonding types have been measured with ex situ spectroscopic ellipsometry, nuclear techniques and infrared absorption analysis. The results point to more dense and hard layers for the larger monomer flows (and thus larger rates). An explanation for the dependence is sought in a variation of the energy flux/deposition event, which decreases with increasing flow. Such an explanation would tend more to a thermal growth picture, but can also fit in incomplete
dissociation and thus more CH$_3$. With toluene admixed with a small amount of CF$_4$ thin layers were deposited on cold rolled steel [30]. It appeared that the corrosion resistance of these layers is very promising. From these experiments it appears that a small admixture of fluorine containing gas is beneficial for the layer properties and leads to a smoother layer. This example again shows that the major hindrance in this field is a good picture of the growth process: it is still nearly impossible to get such a beneficial effect of F-admixture.

Figure 7. (a)–(c) Effect of increasing H$_2$ admixture on the Raman spectrum. with other reactor settings constant: \( \{C_2H_2\}=1; P_{arc} \approx 2.6 \) kW; \( p_c=10^2 \) Pa; \( T_{py} \approx 840 ^\circ \)C; increasing H$_2$ addition, 5, 10 and 20 scc/s respectively.

The Raman peak at 1355 cm$^{-1}$ is called the defective graphite peak (DG), the one at 1581 cm$^{-1}$ the graphite peak (G). Better material corresponds to a large G/DG ratio. (d) Micrograph of the film of (e). In (e) the erosion threshold for amorphous (open symbols) and crystalline (solid) graphite is shown as function of H$_2$ flow. (CFC denotes carbon fiber composites) From Buuron et al. [30], [31].
With the same method also crystalline layers as graphite and diamond can be deposited. Graphite is grown if the substrate temperature is above 600 °C with relatively large amounts of C₂H₂ (8 sccls). Thick layers (up to 2 mm) were grown with deposition rates between 2 nm/s on 30 cm² up to 400 nm/s on 1 cm². The material (for divertor repair) has been tested on erosion threshold (cf. fig. 7) [31]. In fig. 7 the quality improvement of the graphite as measured with Raman spectroscopy with increased H₂ admixture (up to 20 sccls) is also shown. With increasing H₂ admixture the graphite peak at 1581 cm⁻¹ grows and narrows, whereas the defective graphite peak at 1355 cm⁻¹ decreases. It is clearly an example of quality improvement with the addition of etchants, at the cost of deposition rate, which is a quite general feature of plasma deposition.

![Graph showing Raman spectra](image)

**Figure 8.** Raman spectra of diamond films deposited at different pressures. Note that the highest pressure film with the best Raman spectrum (diamond peak at 1332 cm⁻¹ most prominent) grows also faster than the others. For comparison also a single crystal grown with the same method is shown with Raman spectrum from, Beulens [29], [32].

Diamond has been grown by various methods (hot filaments, flames, ECR plasmas, inductive coupled plasmas and thermal arcs). Again the fact that from this variety of methods similar qualities have been obtained points to a more thermal explanation of the growth process. Also with the expanding plasma beam diamond was successfully deposited. Essential are high etchant admixtures (H₂, O₂/H₂) and for CH₄/H₂ a high substrate temperature (1000 °C). In figure 8 results with Raman spectra for 3 ambient pressures are displayed. It is clear that higher pressure gives better quality in this case. The diamond Raman peak at 1332 cm⁻¹ appears and becomes prominent at the highest pressure. At the same time the deposition rate increases to 10 nm/s with pressure because of the narrowing of the plasma beam with pressure [32]. It is another example of improvement of quality together with
improvement of rate.

To complete the section on deposition rate some words should be said about nucleation, cluster and dust formation in the plasma phase. Investigations in silane point to two phases: nucleation and first growth by negative ion (or cluster)–positive ion recombination agglomeration (up to 1–10 nm) and continued growth by association of radicals and monomers to the cluster [33]. Final size and dynamics depend on flow fields and electrostatic potentials. The clusters are negatively charged with charge number roughly proportional to the radius and the major forces are the electrostatic and drag forces. Clusters or powder influence the plasma state and offer an additional wall, probably at a high temperature. Powder may be detrimental e.g. for deposition; it may also be very useful for the production of catalyst and ceramic powder. Also this aspect forms a very interesting and new area for the plasma physics community.

4. Plasma chemical conversion and waste destruction

Conversion processes and waste destruction processes require high throughputs to be economical and hence thermal plasmas at atmospheric pressure high power levels and high throughputs are common in this field [34]. Thermal plasmas have traditionally been used for plasma spraying, element analysis, C<sub>2</sub>H<sub>2</sub> synthesis and for extractive metallurgy [35]. We will further shortly summarize waste destruction and effluent gas purification with plasma technology.

With plasma spraying injected ceramic or metallic powder is accelerated and heated by the plasma emanating from a high power DC plasma gun or from an inductively coupled plasma (ICP) and deposited on the workpiece. The material and energy efficiencies are high with corresponding high growth rates. The process has been investigated in detail [37] with plasma diagnostics and in flight analysis of velocity by laser anemometry and of particle temperature by pyrometry. The new development here is low pressure plasma spraying, with deposition in a lower pressure (0.1–0.3 bar) inert atmosphere. Inductively coupled plasmas (ICP) are used traditionally as excitation source for atomic emission/ion mass spectrometry element analysis. Droplets are injected, evaporized and atomized in the inductively heated plasma; with emission spectroscopy or mass spectrometry the element concentrations of the sample (in the droplets) are measured with very high sensitivity (1–10 ppb).

Waste destruction is relevant for concentrated liquid organic waste, waste from manufacturing processes (e.g. metallic dusts) and low level radioactive waste. For the destruction of liquid organic waste commercial units exist [38] e.g. a 1 MW non-transferred plasma torch with two cylindrical electrodes which allows destruction of PCB's at a rate of 12 l/min (at 850 kW). The process is economical for intermediate amounts of waste, also as the processing unit is self contained and can be moved to the waste site. For larger amounts of waste, incineration is more economic. Combination of plasmas with thermal processing may be way to improve the economics of the total unit. Other technologies under investigation are transferred arcs also of high power combined with rotating furnaces in particular for metal scrap recovery.

Cleaning of effluent gas (De NOX/De SOX) by corona discharges [39], non-thermal plasmas at atmospheric pressure have been shown to be promising, in particular the pulsed negative corona and the silent discharge. Both types have already a history in effective and efficient ozon production.

In all these processes economics is a key factor, which also requires testing (after scaling) at high power levels. The field is still developing; a new development is the realisation that heterogeneous reactions on droplets or dust can be a key factor to reduce the energy cost per conversion and thus the economics of the process. In this area further research on cluster dynamics, electrostatic and drag forces and
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(catalytic) heterogeneous reactions is necessary to investigate this promising line. It is again an example that plasma physics research needs to be complemented with flow dynamics and surface chemistry to fully exploit the potential in the field.

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