

The 2012 Plasma Roadmap

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REVIEW ARTICLE

The 2012 Plasma Roadmap

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Abstract

Low-temperature plasma physics and technology are diverse and interdisciplinary fields. The plasma parameters can span many orders of magnitude and applications are found in quite different areas of daily life and industrial production. As a consequence, the trends in research, science and technology are difficult to follow and it is not easy to identify the major challenges of the field and their many sub-fields. Even for experts the road to the future is sometimes lost in the mist. *Journal of Physics D: Applied Physics* is addressing this need for clarity and thus providing guidance to the field by this special Review article, *The 2012 Plasma Roadmap*.

Although roadmaps are common in the microelectronic industry and other fields of research and development, constructing a roadmap for the field of low-temperature plasmas is perhaps a unique undertaking. Realizing the difficulty of this task for any individual, the plasma section of the *Journal of Physics D* Board decided to meet the challenge of developing a roadmap through an unusual and novel concept. The roadmap was divided into 16 formalized short subsections each addressing a particular key topic. For each topic a renowned expert in the sub-field was invited to express his/her individual visions on the status, current and future challenges, and to identify advances in science and technology required to meet these challenges.

Together these contributions form a detailed snapshot of the current state of the art which clearly shows the lifelines of the field and the challenges ahead. Novel technologies, fresh ideas and concepts, and new applications discussed by our authors demonstrate that the road to the future is wide and far reaching. We hope that this special plasma science and technology roadmap will provide guidance for colleagues, funding agencies and government institutions. If successful in doing so, the roadmap will be periodically updated to continue to help in guiding the field.

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Plasma-etching processes for future nanoscale devices

Seiji Samukawa, Tohoku University

Status. Recent ultra-large-scale integration (ULSI) production processes involve the fabrication of sub-22 nm patterns on Si wafers. High-density plasma sources, such as inductively coupled plasma (ICP) and electron-cyclotron-resonance (ECR) plasma, are key technologies for developing precise etching processes. However, these technologies include several types of radiation damage caused by the charge build-up of positive ions and electrons [1] or radiation from ultraviolet (UV), vacuum ultraviolet (VUV) and x-ray photons [2] during etching. Voltages generated by the charge build-up distort ion trajectories and lead to the breakage of thin gate oxide films, stoppage of etching, and pattern dependence of the etching rate. Additionally, high-density crystal defects are generated by UV or VUV photons radiating from the plasma to the etching surface. These serious problems must be overcome in the fabrication of future nanoscale devices as they strongly degrade the electrical characteristics of the devices and increase critical dimension losses in the etching process. In short, sub-10 nm devices require defect-free and charge-free atomic layer etching processes.

Here, we briefly introduce the electron shading phenomena and a model for them (figure 1) [1]. In high-aspect-ratio patterns, almost all ions can impinge onto the etching bottom between the lines because of their vertical incidence. Since the electron incident angles are usually large, the photoresist shades the etching bottom from these electrons. This shading causes an excessive positive charge flow to the bottom, and results in charge damage and distorted ion trajectories.

During plasma processing, the bombardment of positive ions and irradiation of UV/VUV photons generate high-density crystal defects on the etched surface. The UV and VUV photons with wavelengths less than 300 nm then penetrate MOS devices within a few tens of nm to 100 nm in depth and generate high-density crystal defects (figure 2(b)), positive charges in the dielectric film, and/or interface traps in SiO₂/Si [3], while positive ion bombardment generates defects within

a few nm in depth from the surface [4] (figure 2(a)). That is, UV/VUV photons induce more severe irradiation damage than positive ion bombardment. These defects, positive charges and interface traps cause the degradation of MOS devices by dielectric breakdown, shortening of the lifetime of minority carriers and shifting of the threshold voltage in transistors.

Current and future challenges. Argon fluoride laser (ArF) excimer laser lithography, which has been proposed to fabricate sub-50 nm-scale devices, uses chemically amplified photoresist polymers including photoacid generators (PAGs). Because plasma-etching processes cause serious problems related to the use of ArF photoresists, such as line-edge roughness (LER) [5] and low etching selectivity [5], we have to understand the interaction between plasma and ArF photoresist polymers. We investigated the effects of surface temperature and the irradiation species from plasma and found that ion irradiation itself did not significantly increase the roughness or etching rate of ArF photoresist films unless it was combined with ultraviolet/vacuum ultraviolet (UV/VUV) photon irradiation. The structures of ArF photoresist polymers were largely unchanged by ion irradiation alone but were destroyed by combinations of ion and UV/VUV photon irradiation. Here, UV/VUV photon irradiation plays a particularly important role in the interaction between plasma and ArF photoresist polymers.

Recently, non-planar double-gate metal–oxide–semiconductor field emission semiconductors (MOSFETs) have provided a potential solution for nanoscale complementary MOS (CMOS) technology thanks to their ability to control leakage while maintaining a high drive current. However, the fabrication of vertical Si fins is challenging. With conventional plasma etching, defects caused by the irradiation of charged particles and UV/VUV photons during processing seriously affect device performance and reliability. Surface damage and mobility degradation of the plasma-etched sidewall have already been reported [6].

Plasmas are also extensively used for the etching/ashing of low-dielectric (low-*k*) films. However, since low-*k* films, such as SiOC films, are vulnerable to plasma irradiation, they are severely damaged during plasma processes such as the extraction of methyl groups from low-*k* films. As a result, plasma irradiation increases the dielectric constant of low-*k* films and reduces the reliability of Cu/low-*k* interconnects. The plasma processes change the structure of the SiOC film deep within the film (over 100 nm in depth) and increase the film's dielectric constant. It has also been found that UV/VUV photon irradiation in the plasma etching enhances the extraction of methyl groups from the SiOC film by breaking Si–C bonds in the film [7]. This demonstrates that photon irradiation plays a very important role in the damage mechanism of low-*k* films during plasma processes.

Advances in science and technology to meet challenges. Ultraviolet radiation and charge build-up during plasma processing affect the surface of materials. Nevertheless, the interaction of UV photons and charge build-up with the surface of a given material is not clearly understood because

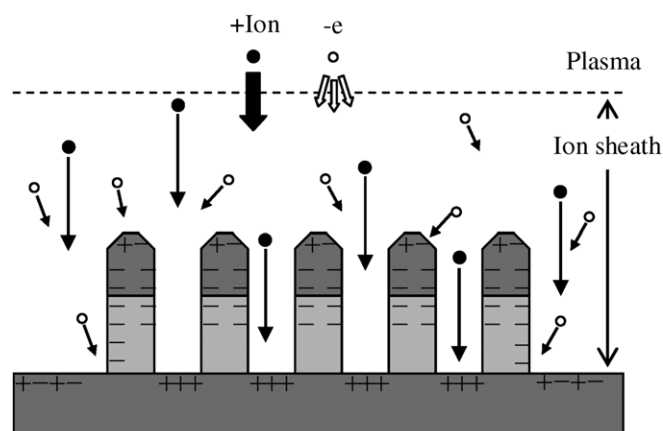


Figure 1. Electron shading phenomena during plasma-etching processes.

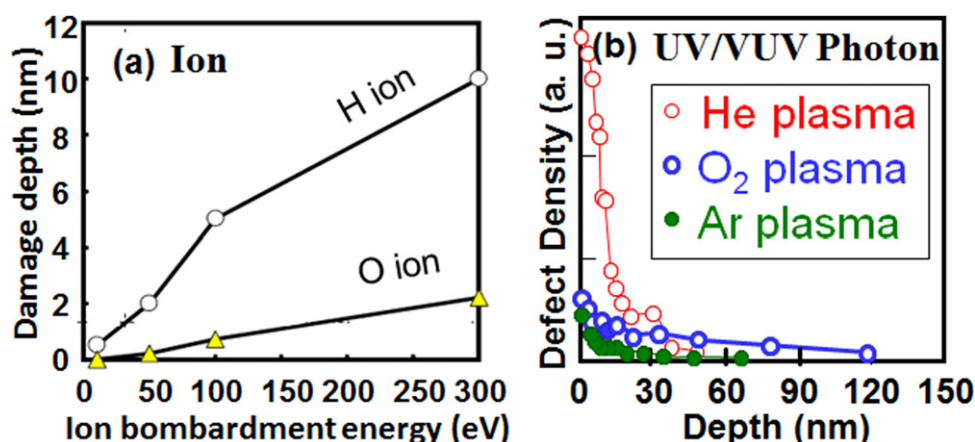


Figure 2. Defect generation caused by (a) ion bombardment and (b) UV/VUV photon irradiation during plasma-etching processes.

of the difficulty in quantitatively monitoring these problems during plasma processing. For this purpose, an on-wafer monitoring technique for the amount of charge build-up and the spectrum of UV photons has been proposed. Additionally, this on-wafer monitoring technique has been combined with a simulation to establish a relationship between the data obtained from the on-wafer monitoring technique and the actual damage [8].

To make a breakthrough in tackling plasma irradiation damage, tens-of-microsecond pulse-time modulated plasma processes [9] and neutral-beam processes [10] have been extensively investigated. The charge build-up phenomena and defect generation due to UV/VUV photons were found to occur at a time constant of 10^{-3} s during plasma etchings. The amount of surface charging and defect generation could be precisely controlled by turning the plasma on and off at a pulse timing of a few tens of microseconds in the pulsed plasma. Conversely, the neutral-beam source completely eliminated the charge build-up and UV/VUV photon irradiation by inserting carbon apertures between the plasma generation region and the substrate surface. In future nanoscale devices, both methods will be very promising candidates for damage-free etching processes. The neutral-beam processes in particular have an advantage in terms of achieving atomic layer defect-free etching while the etching rate is much lower than that in plasma etching. As future nanoscale devices will not need a

higher etching rate, neutral-beam etching has greater potential to create the essential characteristics of nanomaterials and nanostructures.

Furthermore, we think that new materials, such as Ge, GaAs, carbon nanotubes, graphene, bio-supermolecules, e.g. DNA and proteins, and organic molecules, e.g. self-assembling monolayers (SAMs), will be also used for active areas on silicon in future nanodevices. In these devices, extremely low damage atomic layer processes with precise control of generating reactive species and its acceleration energy will be needed to integrate these new materials on silicon substrates.

Concluding remarks. Over the past 30 years, plasma-etching technology has been a leader in the effort to shrink the pattern of ultra-large-scale integrated (ULSI) devices. However, inherent problems in the plasma processes, such as charge build-up and UV photon radiation, limit the etching performance for nanoscale devices. To overcome these problems and to fabricate sub-10 nm devices in practice, tens-of-microsecond pulse-time modulated plasma etching and neutral-beam etching processes have been proposed. These processes can be used to perform damage-free etching atomically and surface modification of inorganic and organic materials. This technique is a promising candidate for practical and accurate fabrication of future nanodevices.

Plasma deposition processes for ultimate functional devices

Masaru Hori, Nagoya University

Status. Applications of plasma for film deposition began with the discovery of sputtering in 1852 by Grove [11]. Chemical vapour deposition (CVD) was invented by Schmellenmeier in 1953 as a method of forming amorphous (a-) carbon films [12], and led to groundbreaking research on plasma polymerization techniques in the 1980s. Even today, CVD remains a highly active area of investigation for producing materials such as diamond-like carbon (DLC), and is applied in a wide variety of fields, such as tribology, biomaterials and photovoltaics (PVs). Silicon thin-film CVD was first reported by Chittick *et al* in 1969 [13]. Such films were amorphous (a-Si) and included a high density of dangling bond defects, thus making them unsuitable for use in electron devices (EDs). This problem was tackled by Spear *et al* in 1975 [14], who used SiH_4 in the Si CVD process. This led to a-Si:H films whose dangling bonds were terminated by H atoms, allowing them to be successfully applied to EDs. *In situ* impurity doping techniques using, e.g., PH_3 gas, opened the door for the formation of pn junctions and fabrication of PVs. Subsequently, the development of the hydrogen dilution process allowed the formation of microcrystalline (μc -) Si films whose quality was sufficiently high for the fabrication of high-mobility devices. Recently, lower process temperatures have been investigated, allowing film formation on flexible plastic substrates. However, despite the remarkable amount of progress that has been made, several issues remain, such as optical degradation and the trade-off between quality and deposition rate (table 1). As a method of achieving atomic or molecular-level control during thin-film deposition, atomic layer deposition (ALD) was developed in 1974 by Suntola [15]. Self-assembly, bottom-up processes represent another approach to achieving precise control of deposited films, and such methods are being intensively investigated with the goal of realizing atomic-scale devices (figure 3).

Current and future challenges. One imminent challenge is the development of methods for rapid deposition of μc - and a-Si films for PV applications. Since the light absorption coefficient of μc -Si is lower than that of a-Si, thicker films are generally required. To be economically viable, plasma-enhanced CVD (PECVD) techniques capable of depositing μc -Si with faster rates of 2.5 nm s^{-1} on larger glass substrates ($>4 \text{ m}^2$) are required. The density of H radicals is a key factor determining the density of SiH_x radicals [17]. One of the major factors determining the deposition rate is the density of SiH_x radicals in the plasma, which in turn depends on the density of H radicals. For this reason, information concerning factors such as the surface loss probability of H radicals is indispensable for numerical simulations and design of large-scale systems, and this has been investigated by measuring the decay of the H afterglow intensity [18]. Recently, plasma-enhanced ALD has attracted considerable attention as a method for fabricating flexible devices at around room temperature. In contrast to this kind of top-down approach, new reaction

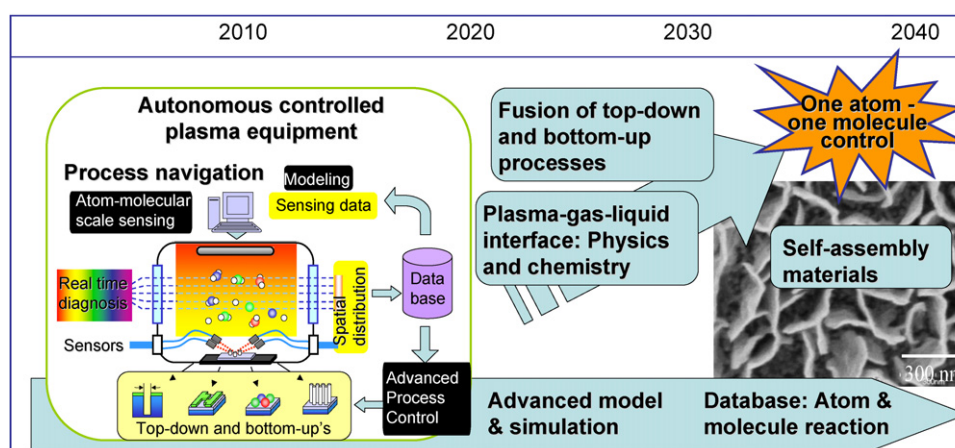
systems for non-silicon materials, such as ZnO and TiO_2 , are also the subjects of increased interest for next-generation green device applications. In addition, development of bottom-up CVD techniques for organic materials such as carbon nanotubes (CNTs) and graphene sheets has also been an area of intensive research in recent years. For such materials, PECVD is also a strong contender since low-temperature growth can be achieved. However, there are difficult problems that remain to be solved with regard to crystallographic control, such as control of the chirality of CNTs.

Advances in science and technology to meet challenges. To fully understand the chemical reaction field in plasma processes, real-time control and monitoring of such processes are becoming increasingly important, in order to allow both observation in space and prediction in time. Realizing these goals requires advances in both measurement and simulation techniques. Diagnosis must be carried out without disturbing the reaction field, and measurements must be instantaneous and have molecular-scale resolution [19]. Construction of ultimate plasma equipment with autonomous controlling on the basis of a self-diagnostic system will be a final goal [20] (figure 3). In addition, to accurately simulate such processes, complex models dealing with multiple scales ranging from individual atoms to the overall equipment must be developed, and high-speed computational resources made available. For deposition of Si- and C-based materials, bottom-up, self-organizing approaches are expected to meet the challenges of achieving high deposition rates without introducing damage. However, achieving the ultimate goal of atomic- or molecular-level control of deposited films requires an expansion of our fundamental understanding of surface reactions. This will involve obtaining basic data on the generation of reactive species such as electrons, ions and radicals, such as cross-sections and reaction probabilities for electronic and photo-excitation of atoms and molecules, and sets of elementary reactions. Moreover, *in situ* evaluation of surface morphology and damage at the material/device level is required. To meet the needs for large processing areas, minimized feature sizes, and the use of atmospheric-pressure plasmas or plasmas in liquids, there is an urgent demand for the development of evaluation techniques that have high spatial resolution and high sensitivity. There is also a need to develop methods for physicochemical control of the flux and energy of the reactive species by generating beams of radicals or neutral atoms that are stable over long periods, which can be applied to delicate or soft materials such as living biological organisms. It is our goal to push forward the frontiers of plasma applications by developing revolutionary methods for depositing and etching materials.

Concluding remarks. Plasma deposition processes allow new aspects of solid and liquid chemistry and physics to be explored. The ultimate goal is atomic- or molecular-level control during device fabrication. To achieve this, a key approach is the fusion of top-down and bottom-up processes based on self-assembly reactions. It is extremely crucial to establish diagnostic methods and

Table 1. Target on CVD technology for fabricating ultimate functional devices.

Requirements	Technological target	Issues
High-speed synthesis and defect-less process (solar cell)	Autonomous controlled plasma equipment	Spatio-temporal control for generation of chemical species with distribution of density and phases
Large area (high definition flexible display)	Navigation assisted process tuning Ultimate controlled beam processes Self-assembled materials	Self-assemble mechanism for no-defect and high-speed synthesis
	Plasma-liquid process	Atomic- and molecular-level detection of reaction field
Stability for production (mature manufacturing)	Atomically controlled process	Multiscale simulation technique
	Real-time monitoring	Database for chemical reactions for gas and surface
	Fusion of top-down and bottom-up	Reaction probability for exited state navigation
	Simulator design for chemical reaction	

**Figure 3.** Technology roadmap of CVD for realizing an ultimate functional device. (Picture of carbon nanowalls as an example for self-assembling material synthesized by CVD [21].).

eventually autonomously controlled plasma equipment for precisely controlling plasma-induced gas–solid and gas–liquid interfaces. Plasma deposition is expected to drive a wide range of future advances in both industrial and academic fields.

Acknowledgments. This roadmap was created with reference to the roadmap [16] prepared by the plasma electronics division of the Japan Society of Applied Physics (JSAP). The

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Very large-area plasma processing

Shahid Rauf, Applied Materials, Inc.

Status. Plasma processing is vitally important for manufacturing of semiconductor chips, flat panel displays and solar panels. Economic considerations have led to a continuous increase in substrate dimensions in these industries. Leading-edge semiconductor manufacturers are now seriously considering 450 mm wafers while the display panel makers have already started using Generation 10 glass substrates (2.88×3.13 m). A typical Generation 10 plasma processing system is shown in figure 4. Plasma etching and deposition processes involved in manufacturing of devices on silicon wafers or glass substrates sensitively depend on radical and charged particle concentrations in the plasma and ion energies at the substrate. Spatial uniformity and tight control of the above parameters become very challenging with growing plasma dimensions.

Most plasma processing is done using radio-frequency (RF) plasmas using RF sources in the frequency range typically from 100s of kHz to over 100 MHz. Due to finite plasma dimensions and wave reflections at boundaries, excited RF fields inherently form standing waves. If the plasma chamber dimensions become commensurate with the excitation wavelength, electromagnetic effects and spatial non-uniformities in RF fields become inevitable [22, 23]. The plasma processes that use low-frequency or dc power sources do not suffer from these electromagnetic effects. However, they often use static magnetic fields which are non-trivial to distribute uniformly over large areas. Spatially non-uniform electric and magnetic fields and related plasma non-uniformities are one of the main technological difficulties in scaling plasma processes to very large substrates.

This short paper discusses the current status of several plasma technologies in use for very large-area plasma processing, highlights techniques that are being used to extend these technologies to larger substrates, and discusses future research trends and needs.

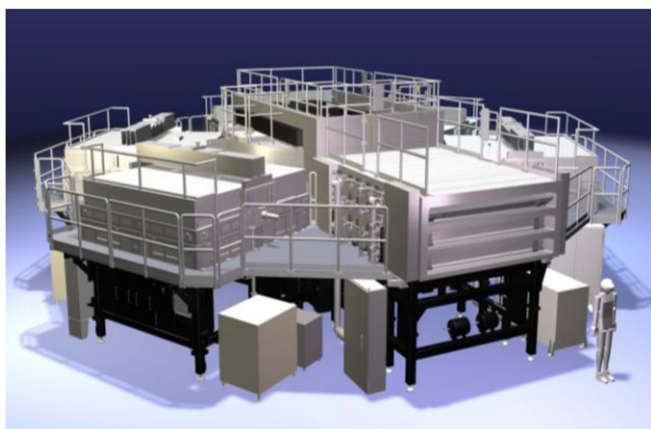


Figure 4. Model of Applied Materials Gen-10 PECVD system (AKT 90K CVD) used for deposition of silicon based films for flat panel displays. The system consists of up to five process chambers, each capable of processing ~ 9 m² large glass substrates. Courtesy of Jozef Kudela.

Current and future challenges. Capacitively coupled plasmas (CCP) are perhaps the most prevalent technology in the processing industry for etching and deposition applications. Many critical applications use very high-frequency (VHF) sources (60 MHz and above) where electromagnetic non-uniformities become prominent on substrates larger than 300 mm. Flat panel display and solar manufacturing technologies use larger substrates, on which the electromagnetic effects impact process uniformity at even 13.56 MHz [22, 23]. These plasma non-uniformities can be suppressed or compensated for by shaped electrodes, multiple RF feeds (or generators), gas flow optimization or by using lower excitation frequencies. For example, non-planar electrodes [24] can modify the electromagnetic field spatial profile and hence the plasma distribution. Generally, these compensation techniques work well for only a limited parameter window, and are often costly to modify with evolving technology.

Another important technology for plasma processing applications is inductively coupled plasmas (ICP). ICPs rely on the electromagnetic power coupling between current in the RF coils and the plasma, and the plasma is generated non-uniformly close to the coils. Furthermore, any RF voltage or current variations along the coils due to electromagnetic effects lead to non-uniform plasma production along the coil. These non-uniformities have generally been addressed through careful antenna design for distributed plasma production and by appropriate selection of RF frequency to minimize the voltage and current variation along the lines. With increasing plasma dimensions, antenna design also needs to ensure that voltage on the coils does not become excessive leading to reliability issues and undesirable capacitive coupling. Scaling of conventional ICP technology becomes increasingly challenging with increasing substrate size, often resulting in complicated antenna designs. A few promising approaches have been developed in research laboratories where electrical non-uniformities along the coils are either avoided using travelling waves with reflection-less line termination [25] or by lowering the operating frequency and using magnetic materials [26].

Microwave plasmas have also been finding applications in large-area plasma processing. With a short wavelength at microwave frequencies, the two general techniques that have been used to obtain large-area uniform plasmas are (1) slot antenna arrays [27], where the array pattern is designed to obtain uniform radiation through the antenna, and (2) travelling wave linear microwave sources [28]. The slot antenna approach requires an antenna design fine-tuned for a particular plasma regime (electron density and collision frequency) and hardware optimization may become prohibitively expensive with increasing plasma size. The travelling wave discharges can be scaled more readily to larger dimensions, although adequate power distribution can be challenging at larger dimensions.

Physical vapour deposition (PVD), i.e. dc, pulsed dc or RF sputtering, remains the dominant plasma technology for metal deposition. Since PVD works well with dc sources, it does not suffer from the electromagnetic non-uniformities. However,

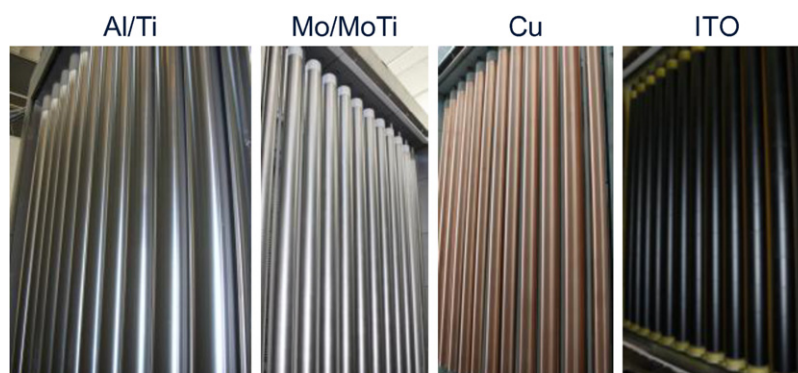


Figure 5. Rotary sputter targets in an Applied Materials PVD system for flat panel display fabrication. Courtesy of Marcus Bender.

target erosion is usually non-uniform due to the non-uniform magnetic field. Not only does the process uniformity become a challenge with increasing substrate size, but also the target cost. Several techniques have been developed to segment targets and increase target lifetime [29]. One such example is illustrated in figure 5.

Advances in science and technology to meet challenges. It is fair to state that the fundamental physics mechanisms governing plasma uniformity in large plasmas are reasonably well understood. The future challenges are primarily technological regarding methodologies that can be used to scale plasmas in an economical manner. Research on new plasma source concepts that can be scaled to larger dimensions more readily is also expected to be fruitful.

One of the most straightforward approaches to extending plasma technology to larger dimensions is to combine multiple smaller sources together. However, plasma is a non-linear medium and coupling between the sources makes operation of multi-source plasmas non-trivial. In addition, where applications dictate small distance between the plasma production region and the substrate, seamless transition between individual sources is non-trivial. One can in principle combine smaller capacitive, inductive, dc or microwave plasmas. In the context of ICPs, a promising recent approach uses an array of ferrite ICPs [30], which addresses both uniformity and high coil voltage concerns for large-area discharges.

Although hardware modifications that compensate for existing non-uniformities can render a tool useful for specific plasma regimes and applications, this practice becomes cost-prohibitive as the plasma dimensions grow. More promising would be approaches that allow dynamic adjustment of plasma uniformity during plasma operation. One such concept is to apply RF voltages at the same frequency but disparate phases to either different electrodes or separate locations on

the same electrode [31]. Phase control appears promising for multi-electrode segmented plasma systems and triode CCP configurations as well.

Electron beam plasmas were developed for large-area substrate plasma processing [32]. Although this technology has not been widely adapted for commercial plasma processing applications, it has promising features for large-area processing. Being a dc technology, it does not suffer from electromagnetic non-uniformities with increasing dimensions. Furthermore, electron energy provides a readily controllable parameter for uniformity control.

Concluding remarks. Economic considerations are driving the plasma processing industry to larger and larger plasmas. Conventional CCP, ICP and microwave plasma technologies all experience uniformity issues when they are scaled to larger dimensions. Electromagnetic effects make CCPs susceptible to non-uniform plasma production with increased electrode size. Although hardware design techniques have been developed to compensate for these non-uniformities, these techniques generally limit the range over which these plasma processing tools can be used. Methods such as phase control, where uniformity can be dynamically controlled during operation, can result in more flexible plasma tools. Similar electromagnetic effects make design of conventional ICP and microwave sources challenging at larger dimensions. Travelling wave ICP and microwave sources appear more promising regarding scaling to larger dimensions. In addition to research on plasma uniformity control methods for conventional plasma technologies, there is an increased need to explore and develop plasma technologies that are more readily scalable to larger dimensions.

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Microplasmas

Kunihide Tachibana, Osaka Electro-Communication University

Status. In general, a microplasma is defined as a plasma of mm to μm size in three-dimensional scales [33–35]. In some cases, however, two-dimensional (linear) and one-dimensional (planar) microplasmas are included. The characteristics of spatial smallness can create new physics, chemistry or science different from those of large-scale plasmas due to the increase in the surface-to-volume ratio. In order to enhance the electron multiplication rate in a shorter distance and also to prevent the wall loss, microplasmas are mostly operated in higher pressure (or density) ranges. Therefore, even if the ionization degree is low or moderate, one can easily make the electron density n_e larger than 10^{13} cm^{-3} [35]. Let us suppose a density of 10^{16} cm^{-3} , for instance, the corresponding electron plasma frequency $\omega_{pe}/2\pi$ becomes about 1 THz. This encourages the use of microplasmas as conductive/dielectric media for electromagnetic waves in addition to the traditional uses such as light-emissive and reactive media, as shown in figure 6 [33].

A microplasma can be used as an isolated device for a localized material processing or biomedical treatment. On the other hand, an assembly of microplasmas is used to construct larger scale devices. It is also aimed at making new functional devices such as photonic crystals or metamaterials with those assemblies [36]. The technologies of integrating microplasmas are also developing [34]. For example, printing technology, such as the one used in manufacturing plasma display panels, is applicable for glass or ceramic substrates and micro-fabrication technology used in semiconductor integrated-circuit manufacturing is effective for silicon substrates.

Current and future challenges. A microplasma can be used as a source for processing various materials: a localized process with a single source and a large-area process with an arrayed source. As a single source, a microplasma jet is the most frequently used device, being driven in wide frequency ranges from dc to GHz. Among such devices a dielectric-barrier-discharge (DBD)-type source, equipped with a pair of ring electrodes around a glass tube of a few mm bore, has become the most popular one because of its simple design. It is

driven by a low-frequency power supply of kHz ranges with a rare-gas flow. One can obtain a long plasma plume of a few cm in length ejected into ambient air. With a high-speed camera observation, however, it appears as if a series of bullets are propagating with an apparent speed of several tens of km s^{-1} . The mechanism is ascertained by various experiments and simulations to be similar to the streamer propagation mechanism in a corona discharge (see [37] and references therein). It has been successfully applied to the deposition of various thin-film materials such as SiO_2 and ZnO . By employing the non-equilibrium and transient nature of a microplasma, it is also applied to the synthesis of nanoparticles [38].

A more enthusiastic concern is directed towards biomedical applications. Stimulated by the pioneering work by Stoffels [39], many reports have been published on the applications of microplasmas for dermatology treatment, surgery haemostasis, dental treatment and so on (see [40] and references therein). In most of these applications, however, we are simply supplying chemically reactive species produced in a plasma to targets for disinfection, sterilization or blood coagulation. In future years, more sophisticated applications are going to be performed such as cellular treatments for cancer therapy and gene transfection.

For larger area processing or treatment, it is required to integrate microplasmas into a large-scale device. This is also true for photonic devices in constructing a large-area light source [41]. Several kinds of sources have been proposed with mesh or fabric structures, bundled jet structures and so on. As a practical example, a plasma stamp with an array of microplasmas on a substrate has been developed for localized material processing in a designed pattern [42].

A more interesting functionalization of a microplasma array is to construct a photonic crystal or a metamaterial for controlling the propagation of electromagnetic (EM) waves. In general, the permittivity of a plasma ε_p is given by [36]

$$\varepsilon_p = 1 - \frac{\omega_{pe}^2}{\omega^2(1 + i\nu_m/\omega)} = 1 - \frac{e^2 n_e}{\varepsilon_0 m_e \omega^2(1 + i\nu_m/\omega)},$$

where ν_m is the electron collision frequency, ω is the angular frequency of electromagnetic waves, e is the electron charge, ε_0 is the permittivity in vacuum and m_e is the electron mass. From this relation it is seen that ε_p can be modified from unity to negative values according to n_e . When we arrange microplasmas in space with a pitch considerably less than the wavelength of propagating electromagnetic waves, we can create a medium whose effective permittivity ε is periodically modulated. As an example, let us think of a two-dimensional array of columnar microplasmas in a square lattice. The relation of ω with the wave vector k is given by the photonic band diagram, as shown in figure 7, according to the propagating direction [36]. It is noted that photonic band gaps appear where the transmission of EM waves is prohibited.

In this extension, by modifying the fundamental parameters of matter: conductance σ , permittivity ε and permeability μ , we will come to an idea of synthesizing a metamaterial from an array of microplasmas. Since plasma itself has no inductance (or permeability), we have to add

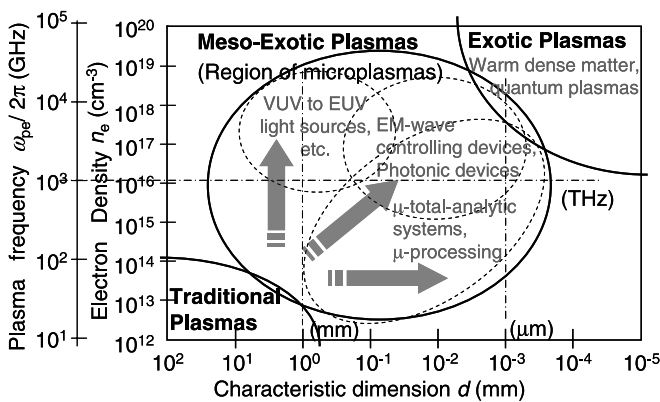


Figure 6. Characteristic area of microplasmas in a plane of spatial size d and electron density n_e .

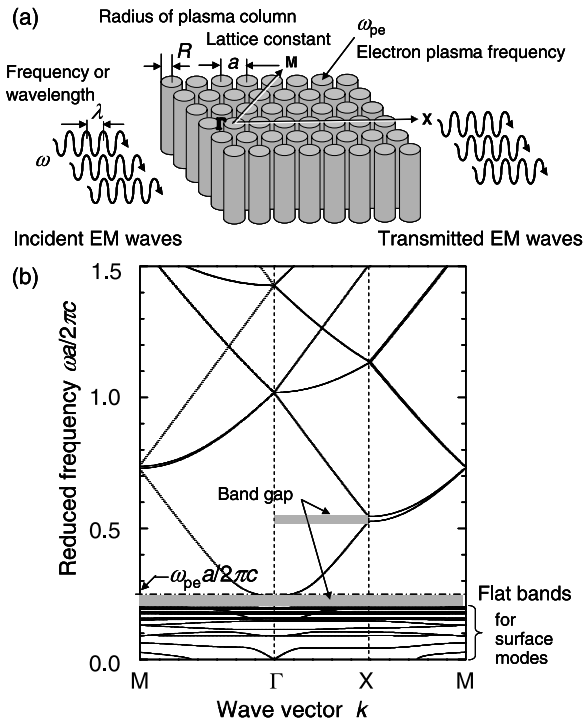


Figure 7. (a) Two-dimensional square lattice array of columnar microplasmas of radius R with lattice constant a , and (b) photonic band structure (dispersion relation); Γ is the origin and X or M is a position at half of the reciprocal lattice vector in the direction shown in (a).

some functional components which can contribute to the spatial modification of μ . For instance, we can make use of the electrode structure for the components, e.g. in the shape of double spiral, split ring, etc. In that manner, we can realize metamaterials with negative refractive index or non-linear bifurcated electric response [36].

Advances in science and technology to meet challenges. As described above, microplasmas are commonly generated

by electrical discharges in higher pressure gases. The discharge media can be generalized as high-density media, including liquids and super critical fluids. In these media the discharge developing mechanisms initiated from a corona discharge should be clarified quantitatively in order to optimize the generation conditions. In particular, in relation with biomedical and environmental applications, the mechanisms in underwater discharges within, with or without bubbles are of much concern.

Plasma–surface interactions are also important research targets for various applications upon well-diagnosed plasma characteristics. In particular, in biomedical applications, the ‘substrates’ exposed to plasmas are living cells, tissues or organisms, so that we have to pay attention not only to instantaneous interactions but also long-range responses stimulated by the irradiation. For basic study on biomedical issues, it is required to miniaturize plasma sources corresponding to the size of a biological cell in order to see cause-and-effect relations of the interaction.

As for the theme of creating new functions by integration of microplasmas, several ideas have been proposed in two-dimensional structures. In most cases, however, microplasmas are actually generated only in pulsed modes. Therefore, generation methods and durable device structures of microplasmas should be investigated for their practical uses in continuous operations. Their extensions into three-dimensional structures will also be of great interest in future.

Concluding remarks. It is frequently asked whether there are any new physics or chemistry of microplasmas in comparison with large-scale plasmas generated in the low-pressure range. To answer the question, some examples have been shown above, which can only be realized by using inherent natures of microplasmas. However, we have to seek more examples by exploring the ‘meso-exotic’ parameter range of microplasmas shown in figure 6.

Plasmas in and in contact with liquids: a retrospective and an outlook

Peter Bruggeman, Eindhoven University of Technology

Status. The first experiments dealing with the interaction of plasmas and liquids date back more than 100 years ago and were conducted in the context of electrochemistry [43]. The same procedure is nowadays still applied to produce nanoparticles at the liquid–plasma interface. Up to about 20 years ago, the main focus in the field of plasmas in and in contact with liquids (PLs) was on glow discharge electrolysis and the study of breakdown of dielectric liquids for high-voltage switching.

Nowadays, it is well established that discharges in and in contact with water are a rich source of radicals, such as OH, O and H₂O₂, and UV radiation [44, 45]. High-intensity plasmas also produce strong shock waves in the liquid phase [45]. PLs thus have strong oxidation and disinfection capabilities and are often referred to as an advance oxidation technology to break down organic and inorganic substances in water. In this perspective the research focus in PLs has been shifted during the last 20 years towards biological, chemical, material and environmental applications. Two reviews, one focusing on the applications [46] and the other on the physics of PLs [47], have been published.

Currently, PLs are generated by nanosecond pulsed and dc voltages. Also, ac excitation from 50 Hz up to MHz frequencies is used [47]. The operation pressures range from very low pressures (using ionic liquids) up to very high pressure conditions in supercritical liquids [48]. Many different reactors exist but the most basic configurations are shown in figure 8.

Electrical breakdown and ionization in liquids have been investigated for several years. Ionization mechanisms in relatively basic liquids such as liquid Ar are well understood [48]. Although it is generally assumed that breakdown in water

occurs through a bubble mechanism or due to the presence of voids [47, 49], all details are not well understood and recently some indications have been found that ionization in pure water without phase change could also be possible.

At this time, we start to grasp the basic physics and chemistry occurring in PLs. Properties of PLs have been investigated extensively [47]. As there is often limited access by laser diagnostics in PLs, mainly optical emission spectroscopy (OES) is used as a diagnostic.

Current and future challenges. Two main challenges can be identified for PLs. The first challenge deals with the breakdown processes and mechanisms in liquids.

The ionization process is of course the first step which needs to be studied in order to understand breakdown in liquids. In dense media, three (and more) body collisions and multi-step ionization processes become dominant. Several unknowns still exist for molecular species and gas mixtures at high pressures.

Plasma propagation dynamics spans time scales going from sub-nanoseconds up to microseconds. Many processes occur on these relevant time scales, i.e. phase change, density, pressure and temperature fluctuations and charge accumulation at the plasma–liquid interface, which makes the propagation an extremely complex physical phenomenon. Additionally, the electrical properties of the liquid can depend strongly on the electrical field, the local density and the frequency components of the applied field. All these effects on the discharge ignition and propagation are to date neither considered in detail nor understood.

The second main challenge is the understanding of the physical and chemical processes occurring at the plasma–liquid interface (see also figure 9). The liquid interface can be an important heat sink. In fact, very strong temperature gradients are observed at the plasma–liquid interface and it remains to be seen if a real connection between plasma at

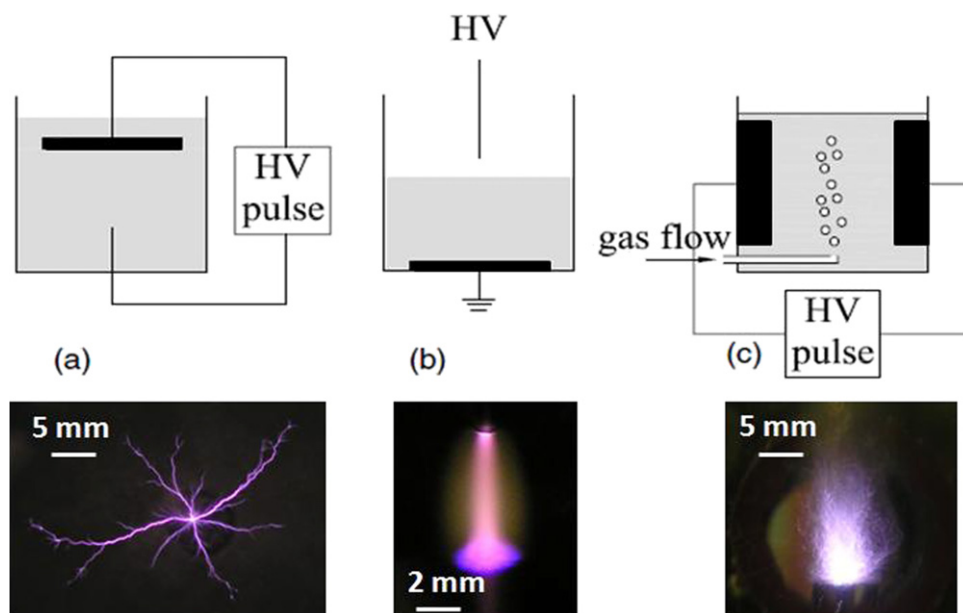


Figure 8. Upper drawings present three basic configurations of PLs. The corresponding figures below are a typical image of the discharge generated in the above configuration. (a) Direct filamentary (microsecond pulsed) discharge in water, (b) dc excited glow discharge (in air) with water cathode and metal anode and (c) (nanosecond pulsed) discharge in (Ar) bubbles in water.

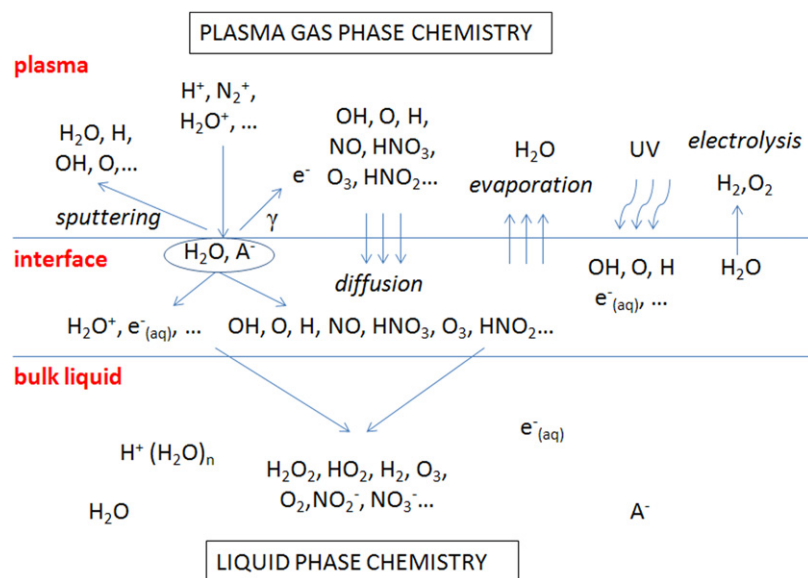


Figure 9. Schematic overview of some important transfer processes at the plasma–liquid interface. Note that some processes are polarity dependent. More details can also be found in [47] and references therein.

a supercritical temperature and liquid water occurs. Apart from the thermal energy transfer at the interface many open questions are still present on how charged species, neutrals and radicals are transferred from the plasma to the liquid phase and vice versa. There exist estimates of secondary electron emission coefficients (γ) based on relations from standard glow discharge experiments, but it is unclear at this time whether the mechanism can be assumed to be similar to the case of a metal electrode.

The understanding of the plasma–liquid interface will allow us to establish a quantitative correlation between gas phase plasma chemistry and plasma induced liquid phase chemistry. This is of utmost importance if one wants to optimize and exploit new application areas.

Advances in science and technology to meet challenges. The key to the understanding of PLs is the further development and improvement of plasma diagnostics to map and quantify the plasma physics and chemistry.

PLs, just like all high-pressure discharges, have very particular issues concerning the interpretation of OES results [50]. Additionally, it is very difficult to obtain quantitative data on radical and ion densities by OES. This is the main bottleneck for a better understanding of the chemistry in PLs. There is without doubt much more information to obtain from OES with more careful interpretations and more evolved models. The collisional radiative models, of course, require an extended knowledge of reaction cross-sections.

However, the possibility of applying active diagnostics even in plasmas in liquids and bubbles would yield much more direct information about the plasma composition. There are several boundaries to be pushed forward to achieve this, especially considering that discharges in bubbles are often surface discharges and that PLs are mainly filamentary, hence mostly not very reproducible in time and space.

More evolved diagnostics in gaseous high-pressure discharges containing water vapour can lead already to more

insights into the (gas phase) water chemistry. As water is electronegative and has the tendency to cause clustering of the ionic species [51] it adds significantly to the complexity of these plasmas.

Diagnostics are also an issue for liquid-based chemistry, especially when dealing with short-lived radicals which are typically composed of the same atoms as water. The time-averaged chemistry (seconds) in the liquid is known and measurable while the plasma chemistry happens on microsecond time scales. It would be very desirable to extend the current bulk liquid techniques—often *ex situ*—to *in situ* techniques with a time and spatial resolution compatible with the plasma size and plasma chemistry time scales.

A further development of the modelling efforts such as presented in [52] by including more detailed physical and chemical processes at the plasma–liquid interface could yield considerable insight into plasma properties which are not easily accessible by diagnostics.

Concluding remarks. In addition to the topics addressed above there are several other interesting research topics concerning injection of liquids in thermal plasmas to produce coatings and powders and laser-induced plasmas in liquids. The strong complexity of driving processes on micrometre length scales and sub-nanosecond time scales in a fluid environment and the highly dynamic plasma–liquid interface provides a wealth of challenging fundamental interesting physics and chemistry for PLs. It can only be unravelled by further development and implementation of state-of-the-art diagnostics and modelling. Note that the understanding of the plasma–liquid interface is also of direct practical relevance, e.g. in plasma treatments of wounds which often have a moist or liquid layer. The effort for the proposed challenging fundamental study will be worthwhile as it will allow us to exploit more efficiently the highly reactive chemistry of these discharges in emerging applications and extend it to new application areas.

Plasma medicine

Gerrit Kroesen, Eindhoven University of Technology, The Netherlands

Status. The field of plasma medicine is, compared with other applications of plasmas, relatively new. Started around the turn of the century at various places around the world in parallel, it has gone through an explosion of attention. In 2007, a dedicated conference series emerged: the International Conference on Plasma Medicine, which will have its fourth edition in 2012 in Orléans, France. Most plasma conferences now feature a session on plasma medicine. Several reviews of the field have been published, see e.g. [53] and all other papers in that cluster issue of *New Journal of Physics*. Impressive results are presented on clinical trials, *in vitro* experiments and cell culture studies. There are indications that plasma medicine can offer solutions for lesions that cannot be treated otherwise, like diabetic feet and other severe ulcers [54]. Most applications focus on the skin, but more recently internal diseases are also tackled. Even the treatment of several forms of cancer is explored successfully [55]. Already since 1996, plasmas have been studied for sterilization purposes [56, 57]. A few studies do shed some light on cell biological aspects [58] (figure 10).

However, there is a remarkable trend: most reports focus on the medical applications, but the dynamics of the plasma itself and the interaction mechanisms between the plasma and the cells, tissues and organisms receive much less attention.

Current and future challenges. Plasma medicine nowadays has the scientific status that plasma etching had around 1980. In the 1980s, the semiconductor industry was already using plasma etching on very large scales in their production processes. That fact has enabled Moore's law to continue to be valid in that period. Nevertheless, the plasma physics community had no idea how exactly the etching process worked. The main research questions focused around things like what plasma deliverables determine the selectivity, etch rate and anisotropy? Around 1990, the large R&D

effort in both industry and academia enabled a much better understanding of the etching process. This understanding has enabled the emergence of remote plasma-etching techniques, where two or more plasmas are used: one to produce the 'plasma deliverables', and one to condition the surface of the semiconductor wafer. Nowadays, this approach is the commonplace technology in semiconductor production. This is an example of where R&D first had to catch up with industry, but later on was able to trigger new technologies. I think that this is true for the plasma medicine community now.

Of course, even more progress in the field of new medical treatments and innovative biological applications (e.g. sterilization) is desirable. However, now we also should address the fundamentals that determine the effectivity of the process. These can be subdivided into three areas: plasma physics, (micro)biology and medicine, and plasma medicine technology development. The main research questions to be answered are as follows.

Plasma physics:

- Where in the plasma are the reactive species, photons and electrical fields produced and what is the production mechanism?
- What are the fluxes and energies of the various species that the plasma delivers to the cells and tissues?
- What is the gas flow pattern?

(Micro)biology and medicine:

- How do bacteria and their signalling, spores, fungi and prions behave under plasma exposure?
- How do animal or human cells behave under plasma exposure? How cytotoxic is the plasma?
- How do human tissues and human beings react when subjected to plasma treatment?

Plasma medicine technology development:

- What is the optimal flux cocktail for eliminating prokaryotic cells?
- What is the optimal flux cocktail for stimulating the recovery of human tissue?
- Which plasma conditions fulfil the best compromise of these two optimums?

Advances in science and technology to meet challenges. Plasma medicine is strongly multidisciplinary: collaboration is required between plasma physics, fluid dynamics, biophysics, microbiology, biology, physiology, medical science and clinical practice. Since we are setting up a roadmap for physics here, we will concentrate on the first three of the above-mentioned disciplines. Plasma physics: diagnostics and modelling.

It will be necessary to determine the densities and fluxes of all plasma deliverables, the so-called plasma cocktail. These deliverables are chemically active molecules (e.g. NO, O₃), radicals (OH and others), photons (especially UV and EUV), ions, electrons and electrical fields. In particular the last one, the electrical fields, is often neglected. Frey and Schoenbach have shown that large fields can cause electroporation and



Figure 10. Example of a plasma in contact with a cell culture.

will in any case modify the ion transport through the cell membrane [59], and even very small dc fields can have effects on cell proliferation and mobility [60]. What is required is a joint action of plasma diagnostics and modelling. The densities and fluxes of all kinds of species will have to be mapped out on the square micrometre. The plasmas that are applied for medical applications in general are small (a necessary consequence of the requirement that they operate at a pressure of 1 atm), of the order of millimetres in at least one dimension. This poses a challenge: most plasma diagnostics that have been developed up to now are compatible with plasma sizes of tens of centimetres and resolutions of millimetres. Now, microscopic resolution is required. Techniques like laser-induced fluorescence (LIF) for molecule and radical detection, Thomson, Raman and Rayleigh scattering for electron parameters, Stark spectroscopy for electrical fields, optical emission spectroscopy for discharge dynamics, and infrared absorption spectroscopy for radical and molecule detection will all have to be enhanced to be able to operate through a (confocal) microscope. Mass spectrometry will have to be carefully engineered to operate at atmospheric pressures and yield results that are actually representative for the plasma just above the sampling orifice. We will also have to address the complication that the plasma parameters will be modified as soon as the plasma contacts the living tissues. In addition, plasma modelling will have to enter a new era. Almost nothing is known about the dielectric properties of cells and tissues, so boundary conditions will have to be revisited. The feedback that the presence of living tissues is presenting to the plasma will have to be addressed (humidity, evaporation, salts, organic substances). Babaeva and Kushner are among the first to address these issues [61].

Fluid dynamics: complex fluids and complex plasmas. The gas flow pattern is an important factor in transporting the active species from the plasma to the patient. Techniques such as particle imaging velocimetry (PIV) and other imaging techniques such as shadowgraphy and Schlieren techniques will have to be operated through a microscope. The flow pattern will have to be modelled as well, and these models have to be connected, and often integrated, with the plasma models. The gas flow may cause cavitation in the liquid on the wound, which may have a beneficial effect or not, but needs to be understood. Cells and small parts of tissues will be removed from the surface of the tissue, and enter the plasma

flow. This will alter the flow dynamics, and may also modify the chemistry. The whole system of plasma, flow, bubbles, droplets and cells is a combination of a complex fluid and a complex plasma: a formidable challenge for fundamental physics.

Biophysics: plasma–plasma interaction. The cell membrane seems to be a dominating factor in the interaction between the plasma and the cell, more specifically between the gas phase plasma outside the cells and tissues and the cytoplasm inside the cell. There is substantial evidence (see [1] and references therein) that Gram-positive bacteria react differently to plasma treatment from Gram-negative bacteria, and the main difference between these categories of prokaryotic cells is the structure of the cell membrane. Furthermore, human cells (eukaryotes) react differently to plasma treatment from prokaryotes, and here again the cell membrane can play a dominant role. In eukaryotes, each internal cell organelle is enclosed in its own membrane. This is not true for prokaryotes, where there is only one boundary separating the plasma from the cell interior. Therefore, we need to study the plasma–plasma interaction through the cell membrane. This field of biophysics is as yet unconnected from the plasma medicine field, but in order to understand what is going on, it is vital to include groups that are active in this field [62].

Concluding remarks. At present, the field of plasma medicine is at the crossroads. Academic and clinical experiments have yielded very promising results. However, the fundamental understanding of the interaction between the plasma and living cells, tissues and organisms is lagging far behind. At the same time, large-scale clinical application of plasma technology is not yet taking off. These two aspects may very well be connected. We can use the analogy of plasma etching described before: in that case industry had no problem in using the technology before it was understood. All that could go wrong is a less favourable process performance. The case of plasma medicine is totally different: human beings are at stake. Without a more profound understanding of the interaction mechanisms, long-term and side effects cannot be predicted accurately. Therefore, we have to establish a multi-disciplinary scientific community to generate this required understanding. After that, large-scale application becomes more likely.

Plasma catalysis

J Christopher Whitehead, University of Manchester

Status. One of the earliest papers reporting the effects of the interaction of plasma and catalyst can be found in this Journal in a review article by Gicquel, Cavadias and Amouroux published in 1986 [63]. They looked at the effect of low-pressure plasma combined with a tungsten oxide (WO_3) surface on both nitric oxide synthesis from molecular nitrogen and oxygen ($\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$) and the decomposition of ammonia ($2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$). They concluded that ‘perturbation of the steady state of the plasma by an introduction of a solid surface has been interpreted as a catalytic action to the extent that it leads to a higher degree of chemical reactivity of the system in question’. Probably, the first account of the combination of an atmospheric-pressure plasma with a catalyst came in 1992 reported by Mizuno *et al* [64], who investigated the synthesis of methanol (CH_3OH) from CH_4 and CO_2 in a dielectric barrier discharge with a $\text{ZnO-CrO}_3\text{-H}_2\text{O}$ catalyst and found that the production of methanol and the conversion of CO_2 and CH_4 were ‘enhanced using the catalyst’. In general terms, the beneficial effects of incorporating a catalyst into a plasma are increased yield of a desired product with high selectivity, i.e. the minimization of other unwanted species. Plasma-assisted catalysis has been shown to have a wide range of applications in environmental clean-up removing common pollutants such as NO_x and VOCs from exhaust gases [65, 66] and in directed synthesis of added value products such as in the reforming of hydrocarbons into fuels [67]. Using atmospheric-pressure, non-thermal plasmas to activate a catalyst can often give significantly reduced operating temperatures (in many cases, close to ambient) compared with conventional thermal catalysis. This can reduce commonly occurring problems of catalyst stability such as sintering at high temperatures, coking or poisoning by species such as sulfur. A synergistic effect is often reported where plasma catalysis achieves a better outcome than the separate effects of plasma processing and thermal catalysis combined. However, this is far from a universal effect and is usually most common at low operating temperatures [68].

Current and future challenges. The complex mechanism of plasma catalysis is far from understood. We can combine plasma and catalyst in two distinct ways: a one-stage arrangement where the catalyst is placed directly into the discharge or a two-stage arrangement with the catalyst downstream of the discharge. In thermal catalysis, heat activates the catalyst but with plasma activation, the electrical discharge supplies the energy. Electron–gas collisions create ions, reactive atoms, radicals, excited species (electronic and vibrational) and photons. In a non-thermal plasma, there is non-equilibrium with high-energy electrons but little heating of the gas. Many plasma-created species are short-lived particularly at atmospheric pressure where quenching, recombination and neutralization are rapid. In one-stage plasma catalysis, all of the species can activate the catalyst. In the two-stage arrangement, only relatively stable species exiting from the discharge will reach the catalyst. These

include gaseous products of the plasma processing and long-lived reactive intermediates (commonly ozone and NO_x in oxygen-containing plasmas). Vibrationally excited species interacting with catalytic surfaces may also play a role [63].

Interactions in one-stage plasma catalysis are either from the plasma with the catalyst or the catalyst affecting the discharge (figure 11). As well as creating reactive species above the catalyst surface, plasma can change the surface properties by ion, electron or photon interactions. Packing catalytic materials into the discharge may modify its electrical properties through changing dielectric effects or by altering its nature, e.g. from filamentary microdischarges to surface discharges [69]. These different interactions may combine to improve catalytic performance.

Figure 12 illustrates the complexity of plasma–catalyst interactions during the processing of a $\text{NiO-Al}_2\text{O}_3$ catalyst with atmospheric-pressure methane plasma [70]. Firstly, NiO is reduced to Ni by the low-temperature plasma ($4\text{NiO} + \text{CH}_4 \rightarrow 4\text{Ni} + \text{CO}_2 + 2\text{H}_2\text{O}$). This is complete when no further CO_2 evolves. Thermally, reduction takes place at temperatures $>400^\circ\text{C}$ but is achieved here at lower temperatures. Hydrogen is then produced with high selectivity by the Ni -catalysed reaction, $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ via the fragmentation of adsorbed CH_4 on active sites of the catalyst surface to form active adsorbed carbon and hydrogen. The carbon appears as nanofibres; a Ni -catalysed process is normally achievable at temperatures $>600^\circ\text{C}$: showing increased energy efficiency for low-temperature plasma catalysis over conventional thermal processing and demonstrating a synergistic effect for CH_4 decomposition, where both plasma and catalyst are vital.

Advances in science and technology. The future applications for plasma catalysis are most likely to be in the area of remediation of gaseous waste and its conversion into products of added value and the use of plasmas to prepare and modify catalysts [71, 72]. A possible form of plasma-catalysis technology for immediate use in environmental clean-up might be a two-stage arrangement using plasma-generated ozone dissociatively adsorbed onto a metal oxide catalyst (e.g. MnO_2) in the presence of a VOC. This has been used for the remediation of benzene and toluene and can be scaled-up for large volume flows [73, 74]. Another scheme selectively adsorbs and concentrates a pollutant onto a catalytic material. The gas stream is then diverted onto another adsorbent whilst the saturated one is treated using a plasma in a one- or two-stage configuration. This has been demonstrated with an oxygen discharge for a range of VOCs adsorbed onto TiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and zeolites [75]. Zeolites were recently used in a cycled storage-discharge process to remove formaldehyde with an oxygen or air plasma [76]. This technique offers many advantages over a continuous thermal system as the cold plasma is only used intermittently for a small percentage of the time required to saturate the adsorbent catalytic material, giving significant energy saving.

Fundamentally, we need to identify the interactions taking place between plasmas and catalysts. Currently, a wide range of spectroscopic and analytical techniques are used

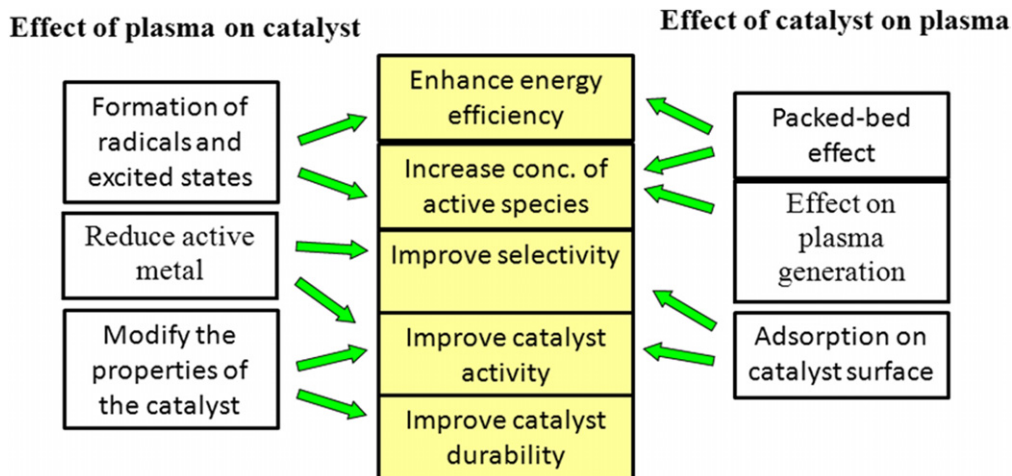


Figure 11. Schematic representation of the way in which plasma catalysis involves both effects of the plasma on the catalyst and the catalyst on the plasma. Adapted from [66].

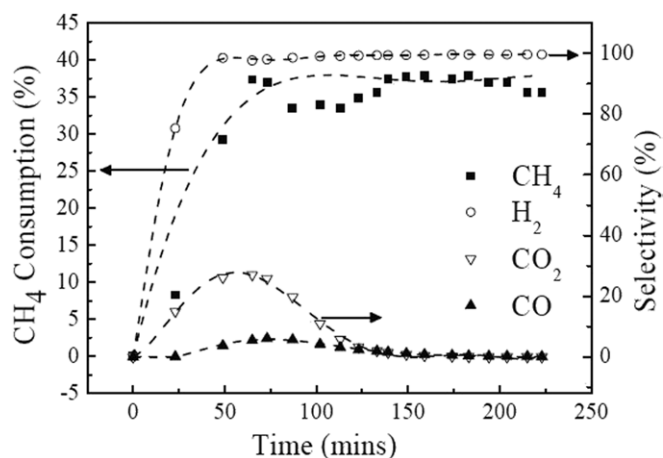


Figure 12. Time evolution of species during the low-temperature plasma reduction of a NiO–Al₂O₃ catalyst to Ni by CH₄ in a dielectric barrier reactor at atmospheric pressure. Reproduced from [70] by permission of Elsevier Ltd.

to identify and quantify the gaseous species including the temporal and spatial profiling of short-lived reactive species within the reactor. The catalyst is generally characterized *ex situ* using surface analysis techniques. We can make some deductions about the role of the catalyst from the gaseous chemistry, by simulation and modelling and from the final state of the catalyst but we need to perform real-time, *in situ* analysis of the surface processes. A plasma is a hostile environment for many conventional techniques for catalyst

characterization but some forms of spectroscopic probing such as reflectance- and ATR-FTIR and non-linear laser techniques that are sensitive to surface species such as second harmonic generation (SHG) and sum-frequency generation (SFG) may be used [77]. Such information will help us to understand the relationship between the gaseous and surface processes taking place in plasma catalysis and to develop more realistic models and mechanisms which could then be used to design catalysts optimized specifically for plasma activation with its lower temperature operation.

Concluding remarks. At present, plasma catalysis is poised to make a breakthrough for a range of applications principally environmental in the broadest sense. Defining the applications in which the technique offers unique advantages will be necessary to construct a roadmap for its development. Certain advantages such as low-temperature operation, high selectivity and improved energy efficiency are clearly emerging. Issues such as scale-up to high throughput processing will be challenging but there is also the potential for small-scale applications based on microplasma techniques using microfluidics such as lab-on-a-chip analysis and flow systems for fine synthesis. Fundamental efforts in probing the surface processes (chemical and physical) taking place will be rewarded by improved modelling and simulation that can be used to design and optimize plasma–catalyst systems for a wide range of processing applications. Engagement with synthetic chemists will produce a range of catalysts that can uniquely exploit the benefits of low-temperature plasma activation.

Thermal plasma applications, including welding, cutting and spraying

Anthony B Murphy, CSIRO Materials Science and Engineering

Status. Thermal plasmas are those in which the heavy-species temperature is approximately equal to the electron temperature (typically in the range 10 000–25 000 K). The plasmas are at or close to atmospheric pressure, and the degree of ionization is high, with electron densities reaching around 10^{23} m^{-3} . Thermal plasmas can be formed by dc or ac electric fields (electric arcs), inductively coupled rf energy, microwave energy or laser energy. The most important properties for industrial applications are (i) the high heat flux density, which can melt metals and vaporize ceramic particles; (ii) the high density of reactive species, which allows high rates of particle formation and surface deposition; and (iii) strong radiative emission, which is used in arc lighting and some mineral processing applications.

Industrial applications of thermal plasmas range from small scale (arc welding, plasma cutting, plasma spraying, arc lighting, circuit interruption) to large scale (electric arc furnaces and other mineral processing methods, waste treatment), with some processes typically on an intermediate scale (nanoparticle production, spheroidization).

Although thermal plasmas have been used industrially for over a century, their applications are a subject of constant innovation. For example, new arc welding techniques are being developed in the effort to increase productivity, involving for example coupling of two arcs (tandem arc welding) or a laser beam and an arc (laser–arc hybrid welding). Even minor increases in welding speed or decreases in cost can be of great significance in industries such as shipbuilding, in which many kilometres of welds are performed daily.

Fundamentally, new variants of established processes are also under development, such as solution and suspension plasma spraying [78], which allow the deposition of thick nanostructured coatings.

Newer technologies, such as nanoparticle production [79] and plasma waste treatment, are increasing in reliability and range of application; for example the conversion of biomass to syngas is generating increasing research interest and application.

While it is impossible to generalize across all the types and applications of thermal plasmas, a number of issues are of broad relevance. These include process control and reproducibility, lifetimes of components (particularly electrodes), scale-up and cost. Addressing these questions requires not only continual process development, but an increase in understanding of many of the fundamentals of thermal plasma processes, as discussed in the next section.

Current and future challenges. An issue of overriding importance is the interaction of the plasma with solids and liquids. Such interactions are fundamental to all thermal plasma applications; indeed most applications rely on the effect

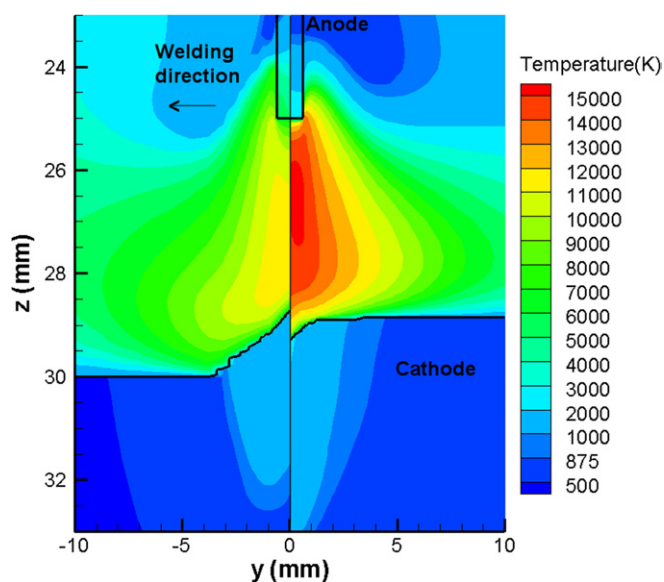


Figure 13. Calculated isotherms in gas–metal arc welding arc and electrodes, including (left) and neglecting (right) the influence of aluminium vapour from the electrodes, for the welding parameters used in [80].

the plasma has on condensed matter. Particular examples include the following.

- In arc welding, production of metal vapour from the electrodes has been found to have a dramatic effect on the arc temperature and a strong influence on the depth of the weld pool, as shown in figure 13. The concentration of metal vapour in the arc and the mechanisms by which it alters the temperature are subjects of controversy [81].
- In plasma cutting, the mechanisms leading to deviations from square cut edges are not well understood [82]; it has been hypothesized that the flow of the thin molten layer is important, but it is also argued that the position of arc attachment (e.g. above or below the workpiece) is decisive.
- In plasma spraying, arc instabilities, which involve the interaction of the arc with the anode, continue to be a subject of research [83]. For solution and suspension plasma spraying, the formation of nanoparticles from the injected liquid droplets is incompletely understood [78].

There have been huge advances in computational modelling of thermal plasmas in the past decade [84], to the point that models are now being commissioned by industry to aid in the design, improvement and scale-up of processes. Nevertheless, comprehensive models of all but the simplest plasma processes do not exist. Sticking points include treatments of vaporization [81], turbulence, radiative transfer [84], arc–electrode interaction including sheaths and boundary layers [85], deviations from local thermodynamic and local chemical equilibrium (LTE and LCE) [86], and nanoparticle nucleation and nanostructure growth [79].

Improvements in existing diagnostics and development of new diagnostics are essential to progress. The challenges are large: for example many applications, including gas–metal arc welding, plasma spraying and plasma cutting, are characterized by rapidly varying temperatures and species densities, often inside hollow electrodes or other structures and

without axisymmetry. Further, plasma velocity measurements are difficult and often unreliable, and current density distributions can only be inferred from measurements made in the electrodes. Due to its small dimensions, the boundary layer between the plasma and the surface has to date proved difficult to measure [85]. An additional challenge is the development of methods to measure the influence of plasmas on surfaces; for example weld pool temperature and shape, and the spreading of a metal droplet as it enters the weld pool.

Finally, most plasma processes involve more than the plasma and its interactions with solids and liquids. For example, metallurgy is critical in welding and cutting, as is the structure of the coating in plasma spraying.

Advances in science and technology to meet challenges. Increased sophistication and accuracy of computational models of plasma processes will require improved understanding of fundamental processes. For example, inclusion of the influence of metal and other vapours in arc models will require more reliable treatments of ablation and vaporization. This in turn requires accurate treatments of heat transfer to the surface by fluxes of charged particles and by radiation. There are several areas in which sometimes severe compromises have to be made between accuracy and tractability. These include treatments of radiative transfer, turbulent flow, nanostructure formation and growth, and the development of the free surfaces at plasma–liquid boundaries.

Understanding of deviations from LTE is still incomplete. For example, the appropriate methods of calculation of the composition and thermophysical properties of a two-temperature plasma are still not clear. Moreover, values of reaction rates at high temperatures, including those of excited and ionized species, are often very approximate, hampering the understanding of departures from LCE [86] and processes that rely on chemistry such as gasification and waste treatment.

The boundary and sheath regions of thermal plasmas remain a subject of controversy. The anode attachment region requires further investigation, particularly in the context of plasma spraying and cutting [85]. Development of a full understanding of the electron emission process in non-thermionic cathodes is incomplete. The standard explanation is thermofield emission, but this requires either electric field intensification or very high pressures; other mechanisms such as emission due to the impact of metastables are worthy of further investigation.

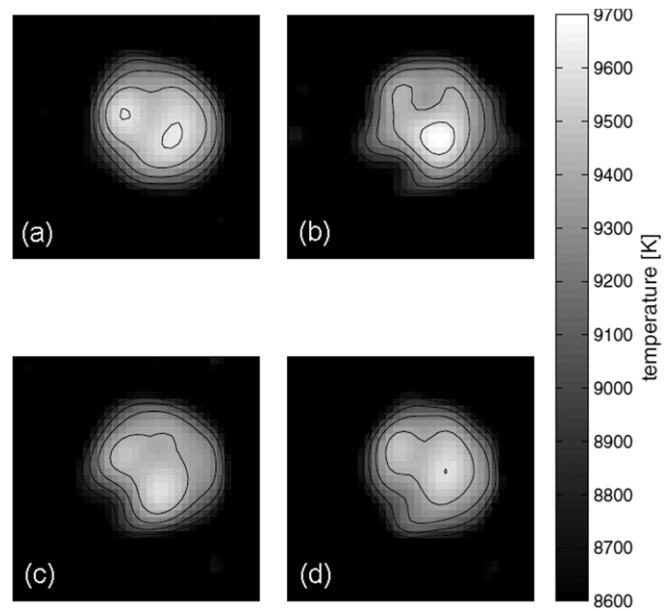


Figure 14. Temperature distributions measured by emission spectroscopy in a cross-section of an argon plasma jet at four times, each separated by $2.14 \mu\text{s}$. From [87].

Advances in diagnostics will require increases in spatial resolution and advanced tomographic techniques; an example of the state of the art is shown in figure 14. Also required are improvements in the ability to measure plasma parameters close to surfaces or in regions obstructed by surfaces, and surface parameters in the presence of intense plasma radiation. While advances in spectroscopic, laser-scattering and probe techniques will all contribute, many cases will require innovative designs for a particular experimental arrangement.

Concluding remarks. It is an exciting period for research into thermal plasma processes. Computational models are increasing in capability and reliability, and predictive models of many processes are within reach. Diagnostics are becoming increasingly sophisticated and powerful. Nevertheless, the continual effort to improve and increase the range of applications of existing processes and to develop new processes requires improvements in our basic understanding of thermal plasmas, and in particular their interactions with surfaces.

Plasma for environmental applications

Alexander Gutsol, Chevron Corporation

Status. Regardless of how strictly we define ‘environmental plasma’, the history and future potential of this technology are quite remarkable. Remember that the oldest and the largest industrial plasma chemical process is ozone production, the main purpose of which is environmental control. Our civilization creates more and more challenging environmental problems (e.g. chemical weapon destruction, dioxins, bio-hazardous waste, etc), where plasma can be a solution and where it can be free from competition with a long-existing and well-developed conventional chemical approach, for the simple reason that the latter does not exist. Several major environmental tasks already have commercially viable plasma solutions: water sterilization and removal of organic pollutants using ozone and/or UV radiation (remember that UV light is generated by electrical discharges); waste destruction and vitrification (including municipal, chemical, radioactive, bio-hazardous wastes and unused weapons); dust and chemical fog separation in electrostatic filters; NO_x and SO_x abatement on a large scale (e.g. power stations) using an electron beam plasma. If we also consider plasma applications that reduce power consumption (which also reduces CO_2 production) and harmful emissions (NO_x , hydrocarbons, soot) during energy conversion as environmental technologies, we should add plasma ignition of coal furnaces at power stations as well as all other plasma ignition and plasma-assisted combustion processes to the list above. Furthermore, plasmas demonstrated significant potential for applications in the following environmental control problems: air sterilization and disinfection [88]; control of air pollutants like volatile organic compounds (VOC), dioxins and mercury in high-volume low-concentration ventilation streams [89]; direct water disinfection and water softening using discharges in water [90,91]; surface sterilization (not only wounds in plasma medicine, but fresh food, vegetables, tables, etc [92]) by different plasmas; reduction of harmful emissions and efficiency increase for internal combustion engines; H_2S conversion [93] and carbon sequestration [94]. Recently discovered ‘plasma acid’ (figure 15, [95]) allows pH control without the use of conventional chemicals and can find applications in water purification processes and water and surface disinfection.

Current and future challenges. There are common challenges for environmental plasmas and many other technologies: energy efficiency, conversion efficiency, throughput, etc. However, in addition, each unresolved environmental task for plasma presents unique challenges. In the case of VOC control, these challenges are of regulatory and technical nature. In the case of automotive applications, plasma system development must catch up with the fast pace of innovation in the automotive industry. On the other hand, the interaction of plasma and liquid or biological material is very far from being well understood. Similarly, efficient H_2S dissociation was claimed long ago; however, the process remains poorly understood and therefore has not yet been commercialized. Although

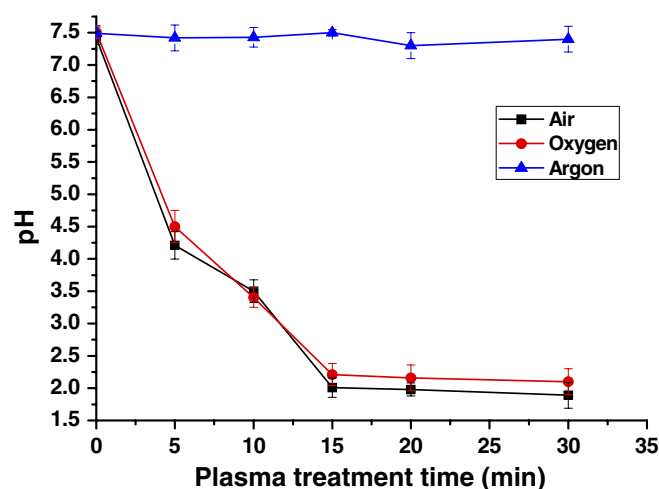


Figure 15. Variations of pH of deionized water after DBD plasma treatment in three different gases [95].

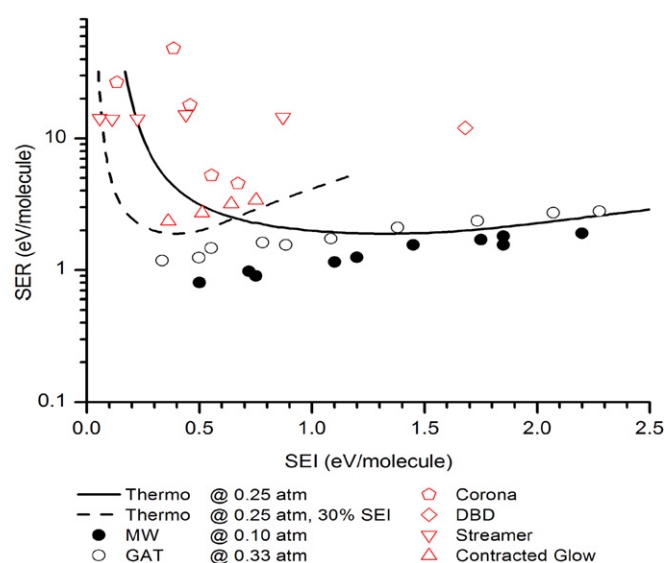


Figure 16. [93] Specific energy requirement (SER) of H_2S dissociation as a function of specific energy input (SEI) for different discharges (including microwave (MW) and Gliding Arc in Tornado (GAT)) and thermodynamic equilibrium model under absolute quenching assumption.

a recent study [93] (figure 16) clarified that only thermally controlled plasma dissociation can be energy efficient, further process optimization and scaling up is necessary. There is a paramount and urgent environmental challenge, to stop or reverse climate changes. Many non-plasma approaches that are under consideration are rather dangerous, e.g. spreading sulfuric acid in the upper atmosphere for controllable cloud formation. Can plasma propose something safe and efficient? Plasma CO_2 dissociation can be rather efficient from the standpoint of conversion of electrical energy to chemical energy, but because of very low chemical energy of CO_2 , this process is attractive only under very specific conditions (e.g. free electrical energy). Energy production with formation of carbon suboxide polymers $(\text{C}_3\text{O}_2)_n$ [94] can be considered as a way of safe CO_2 sequestration, and the formation of carbon suboxides in plasma has been demonstrated by different

researchers; however, it is unclear whether this process can be made commercially attractive using plasmas or any other approach. Safe controlled cloud formation is conceivable using plasmas. For instance, charged water clusters that exist at high altitudes due to cosmic radiation can be collected with the help of solar-powered power supplies of airships, and then this collected water can be electrically sprayed back in the form of larger thermodynamically stable water condensation nuclei. Yet not all technological elements are ready for realization of this process, and neither is the influence of clouds on climate completely clear.

Advances in science and technology to meet challenges. The major advance that is necessary to meet the challenges listed above is the acceptance of plasma as a common tool by the chemical-engineering community. In the United States and probably in many other industrial countries, plasma has been historically considered a mechanical engineering discipline, and therefore, chemists and chemical engineers have very little knowledge on this subject. On the other hand, mechanical engineers who work with technological plasmas and most other people know only about the environmental problems discussed in public media. Meanwhile, there are a lot of problems in different industries that are not well publicized, such as soils polluted with asbestos or hydrocarbons, scrap steel contaminated with mercury, and spreading of invasive marine and river species with ballast water of oil tankers. To bring plasma closer to the chemical and environmental community where it can find more applications, several steps should and can be made. First of all, it is necessary to bring plasma chemistry classes to chemical and chemical engineering departments of universities. To accomplish this, there need to be plasma textbooks for chemists. Plasma books available now are written in physics language and require extensive physics background to be understood. Another approach that can bring plasma to the chemical and environmental industry is the commercial production of reliable, fool-proof, universal plasma systems that can become new tools in chemical labs. Any chemical research lab can and should have in its arsenal

a dielectric barrier discharge (DBD) plasma generator for gas and surface treatment; a 'warm' plasma system based on microwave discharge, atmospheric glow discharge, or microplasma for generation of high fluxes of chemical radicals; corona plasma for low fluxes of radicals and ions; etc. Chemists are ready to use plasma systems when they are made 'plug-and-play', for example inductively coupled plasma (ICP) is now a common part of many analytical devices, and a user of these devices does not need to know what an 'electron energy distribution function' is and why it is so important for plasma characterization.

Scientific and technological advances that are necessary to meet the particular challenges in environmental plasma are rather obvious, so significant progress towards meeting these challenges can be expected. For example, the interaction of plasma and liquid and biological material is the area of very active research that involves non-plasma scientists. There are multiple hypotheses about the way in which plasma 'kills' microorganisms in different environments, and testing of these hypotheses should result in the development of advanced plasma sterilization technologies.

Concluding remarks. Plasma science and technology can and should play a significant role in solving challenging environmental problems. Global environmental problems often require global approaches and actions on the level of scientific and educational communities, as well as governmental and international agencies. However, individual scientists can make a big impact in making plasma science more accessible and widely understood by focusing on appropriate tasks, e.g. writing a plasma book for chemists. Startups and well-established equipment manufacturing companies can also make a shift in acceptance of plasma by chemical and environmental engineering communities. Environmental and chemical tasks can be best solved by engineers and technologists with a relevant background. An initial role of plasma specialists and engineers should be to provide them with tools and necessary knowledge, and then to help them improve and scale up these tools.

Plasma-assisted ignition and combustion

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Status. In recent decades particular interest in the problem of plasma-assisted ignition (PAI) and plasma-assisted combustion (PAC) has been observed. In spite of the fact that the principle of spark ignition has been known and used for more than one hundred years, there are different systems where the use of non-equilibrium plasmas may be of significant benefit.

There are several mechanisms to affect a gas when using a gas discharge to initiate combustion or to stabilize a flame. There are two thermal mechanisms: (1) acceleration of chemical reactions due to gas heating (it is the main principle of spark ignition); (2) flow perturbations, turbulization and mixing due to inhomogeneous gas heating. Possible non-thermal mechanisms include (3) ionic wind, or momentum transfer from the electric field to the gas due to space charge; (4) production of gradients of active species leading to acceleration of chemical reactions non-uniformly in space; (5) excitation, dissociation and ionization of gas by electron impact leading to acceleration/change of different stages of combustion mechanism. These mechanisms or their combination may give a significant benefit for ignition and control of ultra-lean flames and high-speed flows, cold low-pressure relight systems for gas turbine engine (GTE) applications, high-pressure conditions of homogeneous charge compression ignition (HCCI) engine and so on.

Theoretical considerations concerning spreading of boundaries of hydrogen–oxygen mixture ignition under admixture of O atoms can be found in the pioneering textbooks of N N Semenov. Interest in PAI/PAC was re-initiated in the early 1990s by research programs of the US Air Force Office of Scientific Research (AFOSR) connected with fundamental research concerning a possibility to use non-equilibrium plasma for control of combustion in high-speed gas flows.

Current and future challenges. A whole class of pioneering papers that investigate ignition of combustible mixtures in fast gas flows was published in the 1990s. Typically, the authors installed microwave or RF discharges in a supersonic ($M = 2\text{--}3$) gas flow and observed a bright emission due to combustion initiation. A lack of detailed plasma diagnostics can be mentioned as a drawback of these papers although the demonstration of a principal possibility of using non-equilibrium plasmas for ignition of combustible mixtures is an advantage of these studies. A brief review of the first publications concerning PAI/PAC can be found in [96]. An example of recent development of these costly and time-consuming experiments but with comprehensive diagnostics can be found, for example, in [97].

Detailed measurements of integral parameters of ignition/combustion under the action of non-equilibrium plasmas are typical for the second period of research, 1995–2005, reviewed in [96]. Different plasma sources, dc, ac and pulsed, were tested. The ignition delay time and

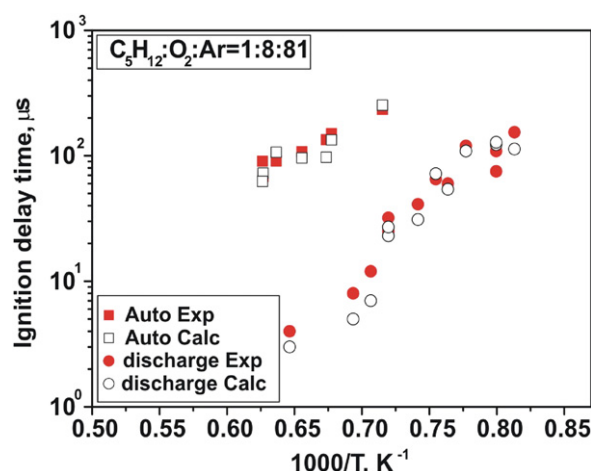


Figure 17. Quantitative data concerning decrease in induction delay time by pulsed nanosecond discharge in a combustible mixture (reference [Kosarev2009] from [99], work of group of Starikovskii at MIPT).

blow-off velocity should be mentioned among the most popular measured parameters. The ignition delay time is determined as the time between the beginning of the experiments, that is gas injection or initial temperature installing, and the sharp increase in densities of species and gas temperature, corresponding to combustion. The blow-off velocity characterizes the stoichiometric ratio of the combustible mixture: the fuel flow decreases until the flame is detached from the flame holder and blown off.

In 1996, a nanosecond pulsed discharge (a few kV/tens of kV amplitude, tens/hundreds of ns duration) was proposed as a tool for plasma ignition. Three key features were indicated as most important: (i) high reduced electric fields (E/N) in the front, up to kTd, provide uniform pre-ionization, so the discharge is homogeneous at relatively high gas densities; (ii) E/N values behind the front, hundreds of Td, guarantee high efficiency of the dissociation via excitation of electronic degrees of freedom; (iii) typical time of production of active species is less than the typical time of ignition/combustion, which allows one to separate in time/space ‘plasma’ and ‘combustion’ problems. This principle has been used in shock tube/discharge experiments (figure 17) where the ignition delay time without/with plasma has been obtained for a set of combustible mixtures simultaneously with resolved in time E/N , current and deposited energy. The publications are reviewed in [98,99]. Nanosecond discharges at $P = 1$ atm in fast repetitive mode (30 kHz) were used for ignition of combustible gas flows at initial gas temperatures $T = 1000$ K [100]. Stabilization of a lean turbulent flame has been demonstrated. Another direction, connected to measurements of ignition parameters at relatively low pressures (up to hundreds of Torr) and detailed measurements of kinetic curves of important components, is reviewed in [101].

Over the last decade, significant progress has been made in understanding the mechanisms of plasma-chemistry interaction, energy branching for discharge plasma of combustible gas mixtures and non-equilibrium initiation of combustion. Analysis of the main factors responsible for the

PAI/PAC [97–99, 101–103] allows the conclusion that at high electric fields in spatially uniform configuration at relatively high initial temperatures the main mechanism of initiation or supporting combustion process is dissociation of molecules via electronically excited states and production of radicals. Partial fuel conversion is observed due to chemical reactions with radicals already on the stage of ignition delay time.

Advances in science and technology to meet challenges. Recently, the ignition of combustible mixtures by transient plasmas has been directly compared with spark ignition [104], and the advantage of multi-point ignition by pulsed discharges was demonstrated. When ignition starts from low temperatures, two processes are considered to be the most important: first, production of radicals by an electron impact, and second, heating of gas due to the developed gas chemistry (in particular, recombination of radicals) and relaxation of energy from electronically excited states (so-called fast gas heating). The length of chemical chains initiated by radicals increases with increase in gas temperature, and so, the ignition occurs. Additional chemistry can be initiated with participation of vibrationally excited or lower electronically excited states. The detailed kinetic mechanism and role of different internal degrees of freedom in PAI/PAC chemistry at different E/N values are still a question of discussion, even for the simplest combustion systems.

Another important question is the development of kinetic mechanisms of PAI/PAC for complex fuels. The cross-sections of collisions with electrons are well known only for the simplest hydrocarbons. This complicates the description of a ‘discharge’ part.

While well-developed combustion mechanisms are known for high temperatures and small hydrocarbons, (GRIMech, RAMEC, Konnov mechanism and others can be mentioned here), there is no accepted mechanism for low initial temperatures. Recent experimental data obtained by different authors and observed in [99] prove that below the self-ignition threshold, at low temperatures, kinetics of ignition development coupled with the kinetics of the discharge can be rather complicated. Standard combustion mechanisms are rarely able to reproduce the temporal behaviour of the main combustion intermediates, such as OH, CH, CN, for the conditions of PAI/PAC. In this sense, detailed experiments and

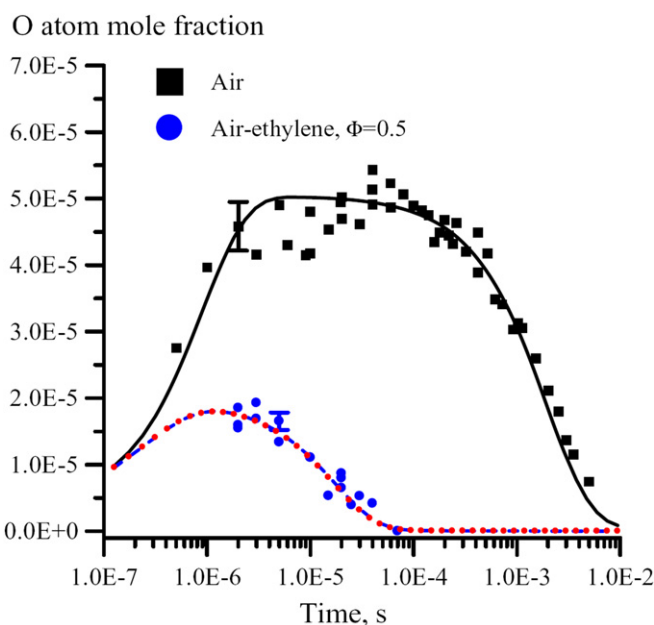


Figure 18. Quantitative data concerning density of O-atoms in air and air-ethylene (ER = 0.5) mixture. TALIF measurements, $P = 60$ Torr, nanosecond pulse energy is 0.76 mJ (according to [20] from review [101]).

modelling on PAI/PAC systems, combining measurements of ‘combustion’ and ‘plasma’ parameters *in situ* (figure 18) with a validation of chemical mechanism are required. As a recent example of such a study, [105] can be mentioned where the influence of low-temperature plasma-assisted oxidation of methane on diffusion flame extinction limits was studied with the help of TALIF, FTIR and chromatography measurements, and the main kinetic paths of excited species and radicals were analysed.

Concluding remarks. PAI/PAC research is a promising application of low-temperature plasmas, demonstrating both high industrial abilities and serious non-solved fundamental problems. Further understanding of PAI/PAC physics and chemistry at low gas temperatures, low equivalent ratios and/or high pressures needs detailed chemical mechanisms to be developed taking into account discharge and combustion chemistry.

'Nanodusty' plasmas: nanoparticle formation in chemically reactive plasmas

Uwe Kortshagen, University of Minnesota

Status. Nanoparticle formation in chemically reactive plasmas has been known for decades. It was initially viewed as a contamination problem in semiconductor processing [106, 107]. However, with the emergence of nanoscience and technology, the ability of dusty plasmas to produce nanoparticles with controlled physical and chemical properties was recognized. Today, it is well understood that particularly for the synthesis of materials that require high synthesis temperatures, such as covalently bonded semiconductors and ceramic nanoparticles, nanodusty plasmas provide a unique synthesis route [108]. Nanodusty plasmas offer several unique attributes based on the exceptional physical and chemical characteristics of plasmas in general, which set them apart from other gas phase media.

1. Nanoparticles immersed in a plasma carry a unipolar negative charge once their size grows to several nm during synthesis [109]. This prevents nanoparticle agglomeration and enables the growth of nanoparticles with highly monodisperse size distributions. It also reduces or eliminates diffusional particle losses to the reactor walls.
2. Particularly in low-pressure plasmas, the combination of energetic surface reactions and slow nanoparticle cooling can cause a strong non-equilibrium [110], in which the particle temperature can exceed the gas temperature by several hundreds of kelvins. This feature is important for the growth of crystalline nanomaterials of high melting point substances.
3. Particle nucleation in plasmas is favoured by the high concentrations of reactive radicals. In some situations it can also be enhanced by the faster rates of ion–neutral clustering compared with neutral–neutral reactions [111].
4. The mixing of several gaseous precursors often enables easy synthesis of alloy materials [112]. The non-equilibrium during nanoparticle growth and synthesis may even allow the formation of compounds that are thermodynamically unstable.

Today, nanodusty plasmas find increasing applications in the synthesis of nanoparticle materials. Successes have been demonstrated in the fields of group IV and III–V semiconductors, carbon-based materials and alloy metal nanoparticles. Some of these successes have translated into new breakthroughs in nanoparticle-based materials and devices in areas such as photovoltaics, light-emitting devices and thermoelectrics.

Current and future challenges (figure 19).

1. Nanoparticle nucleation and growth. The mechanisms that lead to the formation of nanoparticles in plasmas remain poorly understood. Even for particle formation in silane plasmas, which has been studied for more than 20 years, the question whether particle nucleation is driven by neutral–neutral reactions involving radicals or ion–neutral reactions

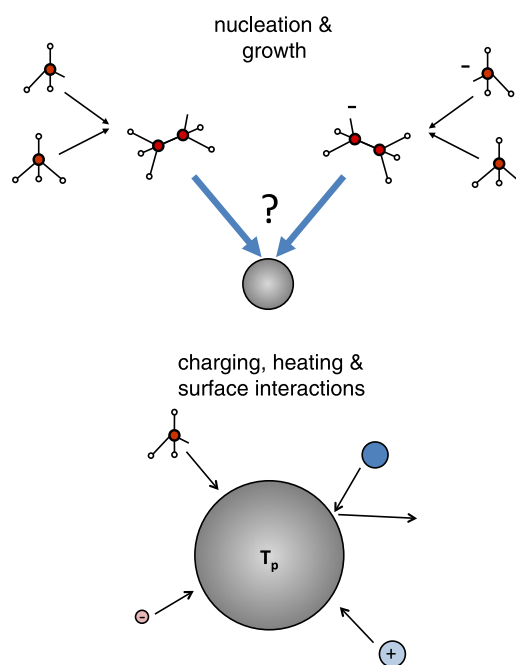


Figure 19. Challenges in understanding nanodusty plasmas: nucleation, growth, charging, heating and surface interactions.

involving negative ions has not been fully resolved. For more complicated materials systems, such as compound semiconductors, not even an initial understanding exists. Better knowledge of growth mechanisms will be essential in being able to control particle properties, composition and purity of nanoparticle materials.

2. Nanoparticle charging and transport. Nanoparticles have a mutual interaction with charge carriers in the plasma. By collecting carriers, particles get charged; at the same time their presence modifies the charge carrier densities in the plasma. For many years, it was accepted that the orbital motion limited (OML) theory correctly described nanoparticle charging. Only recently, researchers learned that collisional effects may cause severe deviations from the OML model, even for nanoparticles that are much smaller than the ion mean free path [113]. Charge fluctuations also play a significant role for nanometre-sized particles. Furthermore, particle charging in multi-component plasmas is almost entirely unexplored. Developing an understanding of particle charging is a prerequisite for developing models for nanoparticle transport and heating in plasmas. A better comprehension of these mechanisms may open up new routes to actively control and manipulate nanoparticles in plasmas.

3. Plasma–nanoparticle surface interactions and treatment. The interaction of plasma species with the nanoparticle surfaces is another largely unexplored area. Plasma–nanoparticle surface reactions are the source of energy for nanoparticle heating that plays a crucial role in the particles' microstructure, e.g. whether particles are crystalline or non-crystalline. Details of the particles' interaction with impacting ions may also explain why the defect densities of nanocrystals prepared with seemingly similar plasmas can differ by two or more orders of magnitude.

For nanoparticles to achieve their full potential, their surfaces must be treated to terminate surface defects, protect nanoparticles from environmental impact (e.g. water, oxygen), and impart new surface functionalities such as solubility in various solvents. In order to achieve these goals, novel plasma approaches are needed to deposit organic and inorganic films on nanoparticles, functionalize their surfaces with organic monolayers and tailor the nanoparticle surface chemistry.

Advances in science and technology to meet challenges.

1. Nanoparticle nucleation and growth. Addressing this challenge will require unravelling the rather complex chemical kinetics in chemically active low-temperature plasmas. Both computational and experimental investigations will be needed to achieve this goal. Expanding the methods of chemical kinetics to plasma environments will require determining the thermophysical properties of radicals as well as ionic clusters and determining clustering reaction rates [114]. Many of these will likely be specific to the materials systems studied. On the experimental side, models need to be validated with measurements of growth species concentrations and particle nucleation and growth rates. This will require measurements of ionic and radical species with methods such as optical emission and absorption spectroscopy, laser fluorescence methods, mass spectroscopy, as well as measurements of nanoparticles in plasmas, for instance, by laser scattering. For very small particles, light scattering may be inefficient and may require the development of novel particle probes.

2. Nanoparticle charging. Several theoretical approaches have been developed to describe particle charging. Some of these models involve particle-based simulations of ion collection by nanoparticles coupled with Monte Carlo collision dynamics. However, there is little experimental verification of these

models. While measurements of the average nanoparticle charge have been reported, there are currently no experimental studies of the particle charge distribution, which becomes increasingly important for smaller nanoparticles that may become bipolarly charged. Developing novel probes to study charge distributions of nanoparticles in plasmas would be of great benefit.

3. Plasma–nanoparticle surface interactions and treatment.

In situ methods to study surface conditions of nanoparticles in the plasma would be invaluable tools to unravel the plasma–nanoparticle surface interactions. Such techniques may be based on infrared absorption of surface species or possibly on fluorescence techniques. Such methods may also enable *in situ* investigation of the nanoparticle temperature, which may allow validating models of particle heating. Developing novel techniques for plasma–nanoparticle surface treatment may considerably expand the utility of plasma-produced nanomaterials for applications. Such approaches may involve the deposition of layers or nanoparticle surface modification in dual or multistage reactors. Again, developing these approaches would benefit from *in situ* characterization techniques, possibly based on infrared, x-ray or Auger electron spectroscopy.

Concluding remarks. Nanodusty plasmas are intriguing both for their multi-faceted physics and chemistry as well as for the significant opportunities to use plasmas as sources of new nanomaterials. There are significant challenges as some of the most basic aspects of nanodusty plasmas, such as particle growth, charging, heating and plasma–nanoparticle surface interactions, are still little understood. The development of novel computational and experimental techniques for the study of nanoparticle–plasma interactions could significantly advance the field.

Plasma thrusters

Jean-Pierre Boeuf, LAPLACE

Status. Electric propulsion (EP) systems can offer much higher propellant velocities than chemical engines, thus allowing considerable propellant mass saving and launching cost reduction. The thrust of plasma thrusters is lower but a combination of low thrust and high specific impulse is sought in several types of missions such as orbit insertion, attitude control and drag compensation.

EP was conceived about 100 years ago and the first use of EP systems on commercial spacecraft started in the last two decades of the 20th century [115]. An overview of the different EP concepts currently studied is given in [116]. Reference [117] discusses in detail the physics and technology of two leading EP systems, the ion and Hall thrusters. A more recent review on the physics of plasmas for space propulsion can be found in [118]. The research on plasma thrusters is extremely active and concerns basic scientific as well as technological issues, as can be inferred from the papers presented at recent International Electric Propulsion Conferences [119].

Plasma thrusters can be electrothermal, electrostatic or electromagnetic, depending on the mechanisms providing the thrust. In electrothermal thrusters a gas is electrically heated (e.g. by an electric arc, as in arcjets) and expanded through a nozzle. Since the expansion of the propellant is purely thermal, they have the same limitations as chemical thrusters. Electrostatic acceleration is well illustrated by gridded ion thrusters (GITs) which are plasma sources where ions are extracted and accelerated out of the plasma by a system of biased grids. A large variety of low-pressure plasma source concepts can be adapted to GITs: dc discharge with magnetic confinement, rf inductive discharge, microwave discharge at electron cyclotron resonance. Electromagnetic (EM) thrusters (e.g. Magnetoplasma-dynamic thrusters, MPDTs) use the Lorentz force $\mathbf{J} \times \mathbf{B}$ due to an external or self-magnetic field acting on the discharge current to generate the thrust. Pulsed Plasma Thrusters (PPTs) are small EM thrusters with a much lower average power than MPDTs.

A very successful concept, the Hall effect thruster (HET) can be considered both as a gridless ion source and an electromagnetic thruster. In HETs, the electric field E accelerating the ions is a consequence of the Lorentz force due to an external magnetic field B acting on the $E \times B$ Hall electron current. The typical thrust for an efficient HET is 60 mN kW^{-1} . The propellant velocity required for geostationary orbit maintenance is around 20 km s^{-1} (corresponding to an accelerating potential of about 300 V for xenon ions).

Current and future challenges. Among the EP systems described above, arcjets, GITs, HETs and PPTs have already a long history of space flight operations and are currently in use in a number of commercial (telecommunications) and government spacecraft. In these applications the electric power used is on the order or below a few kilowatts and the thrust from millinewtons to hundreds of millinewtons. Some of these concepts are still the object of intense research often involving

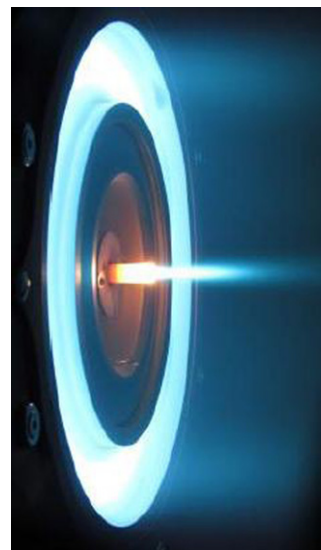


Figure 20. Hall effect thruster PPS-20k ML operating at 23.5 kW, developed in the frame of the FP7 HiPER project [120].

basic scientific issues. Below is a (non-exhaustive) list of challenges.

- (1) Performance improvement: efficiency, lifetime and cost-effectiveness. Lifetime is an important issue and is limited by electrode or wall erosion. Lifetime of an electric thruster must be larger than 10 000 h of (reliable) operation.
- (2) Design of more versatile thrusters, i.e. able to operate at different combinations of thrust/propellant velocity.
- (3) Extension of domain of operation to lower power (μN to 10 mN thrust range) for micro-satellites or very precise attitude control.
- (4) Extension to higher power for orbit raising of telecommunication satellites (several tens of kW) and interplanetary missions (100 kW and more).
- (5) Extension of EP to low-altitude spacecraft: there is an increasing interest in civil and military spacecraft flying at altitudes around 100 km where the drag is significant and must be constantly compensated.

Historically, research in EPs has been focused on electromagnetic thrusters such as MPDTs. HETS and GITs are now starting to compete with these thrusters for high-power propulsion ([120] and figure 20). The need for high-power EP in telecommunication satellites for full orbit raising and orbit transfer is expected to increase rapidly. Advances in solar power generation systems are increasing the total amount of available on-board power, and EP-based orbit transfers using 50 kW or more of electric power are becoming realistic. Work is still needed to design and optimize electric thrusters (GITs, HETs or other concepts) operating reliably in this power range. Interplanetary missions require power on the order of 100 kW and above and such a power can be provided only by nuclear reactors. MPDTs are designed to operate in this power range but the main issue is still the lifetime (fast electrode erosion). Research on electrodeless electromagnetic thrusters is active.

To measure the current interest in the different types of EP systems, it is interesting to look at the number of

papers devoted to each type. At the 2011 IEPC [119] in Wiesbaden, Germany, about 40% of the papers were devoted to HET research (including cusped-field thrusters), 15% to 'unconventional' (not yet mature) thrusters, 10% to GIT, 8% to PPT, 8% to MPDT, 5% to microthrusters, 5% to cathodes (cathode neutralizers are an important part of ion thrusters), 4% to electrospray and field emission electric propulsion, 3% to arcjets and 3% to questions related to the interaction of the plasma generated by the thrusters with the satellite.

Advances in science and technology to meet challenges. As seen above, the research on HETs is extremely active. In spite of the long experience on HETs, their design is still semi-empirical because electron transport across the magnetic field barrier is not well understood. Efforts in the development of kinetic simulations and sophisticated diagnostics must be pursued to fully understand the respective contribution of microturbulence [121] and wall effects [122] (secondary electron emission) to electron transport in the channel. There is still no model able to self-consistently predict electron transport in a HET and to guide the design of the magnetic field. Erosion of the ceramic channel walls (generally BN-SiO₂ type) of the thruster by the plasma is an important issue for its lifetime. In order to perform more systematic optimization of the nature and structure of the wall material, it is essential to develop diagnostics (possibly combined with simulations) that could predict wall erosion without long and expensive life tests. Grid erosion is a major life-limiting factor and cannot be avoided in GITs but with careful grid designs lifetimes longer than 20 000 h have been achieved. In HETs it seems that optimization of the magnetic field design (e.g. by magnetic cusps, as proposed in HEMPTs and DCFTs, see [118] and references therein) could help increase the lifetime even further. Electrode, grid or dielectric wall sputtering is a concern in many EP devices, and systems where these effects are absent are quite attractive. This is the case in devices where a high-density plasma expands through a magnetic nozzle. The magnetic nozzle is a divergent external magnetic field and the thrust is due to the $J \times B$ force, as in HETs, except that J is the azimuthal current due to $E \times B$ drift in HETs while it is due to the diamagnetic drift $\nabla P_e \times B$ in a magnetic nozzle (P_e is the electron pressure). In contrast to HETs the plasma expansion is current free in a magnetic nozzle (no need for a cathode neutralizer). Helicons can be efficient plasma sources for expansion through a magnetic nozzle, leading to an helicon thruster HelT ([118], and IEPC-2005-290 in [119]). The potential and applicability of this 'unconventional' concept are

still to be demonstrated. Plasma acceleration by the effect of a diverging magnetic field alone seems however limited. The VASIMR thruster [123], a well-publicized, megawatt-class EP device, is also composed of a helicon source with a magnetic nozzle, but with an ion cyclotron resonance (ICR) heating module in between, which can provide much higher velocities than the HelT alone. The ICR module requires large magnetic fields, making implementation of this concept rather complex.

From a more general point of view, basic research is needed to address the following (not independent) questions: 'equipotentialization' of the magnetic field lines (see, e.g., the discussion in [124]), the effect of magnetic field cusps on beam divergence, and plasma acceleration through a diverging magnetic field. Other needs for research in EP systems include the question of an alternative propellant: xenon is used in most HETs and GITs because of its large mass and relatively low ionization threshold. Xenon is rare and very expensive and argon would be more appropriate for systematic use in EP systems. Using argon instead of xenon in HETs is not straightforward because ionization is less efficient and implies completely new scaling and magnetic design of the thruster. It may also be necessary to use a complementary ionization stage (double stage HET) to maintain good efficiency. The question of double stage HETs has been previously studied ([118] and references therein) but with limited success and deserves to be revisited.

For low orbit satellites, air breathing thrusters seem very attractive and research is needed to conceive or adapt plasma thrusters for operation under these conditions. Hollow cathode neutralizers are used on most HETs and GITs. New cathode concepts (plasma cathodes) must be studied for low-altitude satellites because hollow cathode materials are very sensitive to oxygen contamination. Specific plasma cathodes must also be developed for ion microthrusters.

As described above, the need for basic research in already mature EP concepts is still considerable. This should not prevent researchers from exploring different and innovative ideas, e.g. electrostatic wave heating or ion-ion thrusters (see papers IEPC-2011-212 and IEPC-2011-130 in the Proc. of the 2011 IEPC [119]).

Concluding remarks. Electric propulsion is a very exciting and active research field. The need for basic plasma physics research is important to improve the performance and extend the domain of operation of EP systems that are already in use on commercial spacecraft as well as to develop new concepts and new plasma sources specifically designed and optimized for EP.

Plasma lighting

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Status. Plasma lighting includes both ‘general’ lighting of spaces like offices, stores and outdoor areas, and also a wide range of ‘specialty’ sources from germicidal lamps to extreme-ultraviolet sources for lithographic patterning of semiconductors. Efficient conversion of electricity into light for human vision motivates work to improve general light sources. Specialty sources share the property of other plasma devices and processes, in that they are complex and used where they uniquely provide some needed benefit. Background information can be found in [125].

For general lighting the importance of efficiency occurs at both the user and the global scale. For a user, electric power accounts for typically 80% of the total ‘cost-of-light’ to illuminate a space, the remainder being the costs of installation, replacement lamps and maintenance. At the global scale the total electricity consumption by lighting is large, equal to the total output of hundreds of large (gigawatt) power plants. So it is the case that even a desirable improvement such as the elimination of mercury from plasma light sources is not sufficient to allow its widespread use if that new light source is also less efficient.

Current and future challenges. State-of-the-art general light source products have an efficiency that is <30% of the maximum possible value of $\sim 400 \text{ lm W}^{-1}$ for white light of reasonable colour quality (colour rendering index >80). There are two primary energy losses that limit the overall efficiency in current plasma lamps (figure 21), and point out the direction for research. In fluorescent lamps more than half of the

power is lost when the plasma radiation (the mercury atom intercombination line, wavelength 254 nm, $\sim 5 \text{ eV/photon}$) is downconverted to visible radiation (wavelengths 400–700 nm, $\sim 2.2 \text{ eV/photon}$ average) [126]. By way of contrast, high-pressure (3–30 atm) metal-halide plasma lamps desirably and efficiently emit radiation directly into the visible. Undesirable plasma infrared radiation can be a significant power loss from such plasmas [127]; it can only be reduced by modifying plasma chemistry and conditions. The persistent unaddressed power loss mechanism in high-pressure lamps is simple heat transfer from the hot core of a thermal plasma ($\sim 4500 \text{ K}$) through the gas to the wall ($\sim 1000 \text{ K}$).

These two energy loss mechanisms have motivated work on non-equilibrium low- and medium-pressure plasmas that have lower heat conduction losses (because there is no thermalized hot plasma core) and in plasma chemistries that emit radiation closer to, or even in, the visible, so as to reduce downconversion losses. Low-pressure metal-halide plasmas in halides of gallium, indium and other metals emit radiation that is closer to 400 nm ($\sim 3 \text{ eV/photon}$, primarily from the metal atom), thereby halving the downconversion loss. Several chemistries operate stably at wall temperatures <200 °C, thereby reducing thermal loss. They have shown promise, but have not exceeded the overall efficiency of mercury [128]. Highly efficient visible-light-generating plasma chemistries have been reported [129], and efficient conversion directly into near-ultraviolet and visible radiation has recently been shown from strongly bound transition-metal-oxide molecules in medium-pressure plasmas [130]. All of these chemistries [128–130] are free of mercury. A reading of the literature cited in these references will give some idea of the practical challenges of finding efficient plasma chemistries with the desired emission spectra, maintaining a suitable vapour pressure of emitting materials in a relatively cold envelope, developing compatible electrodes and phosphors, and combining it all into an economical new product that exceeds what is now available.

Some examples will have to suffice, to represent the diversity of specialty plasma lighting. The first example is light sources that emit radiation in the germicidal wavelength range 240–290 nm. Such lamps are used to purify water for drinking, and also air, and can be an alternative to the undesirable use of oxidizing chemicals like chlorine [131]. Low- and medium-pressure mercury sources are an ancient but unbeaten technology for this application, because no other source can produce germicidal radiation with the combination of efficiency and power density of mercury. There are few other atoms or molecules that emit significant radiation in the germicidal range. The second example is the ultra-high-pressure mercury lamp used for video projection in home theatres, conference rooms and cinemas [132]. A mercury plasma is unique in this application, for its ability to provide a very compact ($<1 \text{ mm}^3$), high luminance ($>10^9 \text{ cd m}^{-2}$) source through a combination of high pressure ($>150 \text{ atm}$) within the temperature limits of a vitreous silica ‘quartz’ envelope ($<1500 \text{ K}$), high visible opacity of the emitting mercury atom, and a high ionization potential leading to high plasma temperatures ($\sim 8500 \text{ K}$, for maximum radiation within

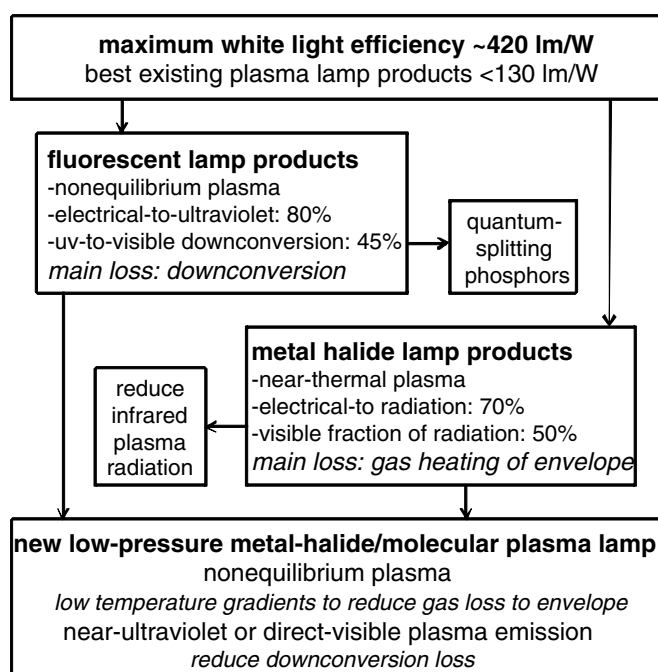


Figure 21. Quantification of energy loss mechanisms in existing high-efficiency plasma lamps points to research topics for future light sources.

the limits of a thermal-blackbody radiation source). The fact that mercury is the material of choice in fluorescent and germicidal lamps (mercury pressure 5 mTorr), metal-halide lamps (3–30 atm) and video projection lamps (>150 atm) gives some indication of its unique properties, and the difficulty of replacing it. A final and unique example of a specialty plasma light source is the extreme-ultraviolet (EUV) plasma under development for next-generation semiconductor lithographic patterning, beyond the current 193 nm excimer lasers. In EUV sources, a plasma of multiply ionized tin atoms is the source for radiation at 13.5 nm (92 eV). Continued development of this most difficult technology is justified simply by the fact that there is no other known means to produce hundreds of watts of EUV radiation [133].

Advances in science and technology to meet challenges.

Experimental development of new plasma light sources is a multidisciplinary effort that usually entails (i) handling corrosive chemicals in an oxygen- and moisture-free environment; (ii) sealing the desired chemistry into corrosion-resistant envelope materials such as translucent alumina; (iii) maintaining a minimum temperature on all inner surfaces during operation, to prevent undesired condensation; (iv) coupling electrical power through chemically and mechanically stable electrode feedthroughs, or via high-frequency capacitive or inductive excitation; (v) accurately accounting for power losses and estimating the power that is coupled into the radiation-generating portion of the plasma; and (vi) accurately estimating the radiant flux—that is, the absolute total radiation into all angles over a wavelength range 200–800 nm. Any eventual high-volume lamp product will be highly engineered towards simplicity, but a flexible laboratory capability to explore new plasma chemistries and operating methods is not easily assembled and maintained, even for relatively ‘conventional’ general light sources. The need for accurate measures of absolute input power and output radiation should not be underestimated; even calibration standards are lacking, in some cases. The development of specialty light sources brings additional requirements that are particular to the intended application.

Mechanistic computational models and experimental characterization provide an understanding of the operation of plasma lamps, and form the basis for insights and breakthroughs. As is the case in some other plasma specialties,

the limitation is often not the plasma model, but rather a serious lack of input data for each new chemistry—reaction mechanisms, cross-sections, rate-coefficients—both in the gas phase and on surfaces. The growth of semi-empirical and approximate methods to estimate such data has therefore been key to timely generation of plasma modelling results, and to the associated mechanistic understanding [128, 134].

Difficulties with optical access to lighting plasmas, even idealized laboratory versions, tend to reduce the usefulness of detailed time- and space-resolved optical characterization, and lead to a productive emphasis on classical spectroscopic analysis of integrated lamp emission spectra [128]. In fact, the combined use of such models and characterization methods is best, where the strengths of one approach can be used to fill the gaps of the other.

Concluding remarks A legitimate question can be raised about the future of plasma light sources, in view of the growth of solid-state light sources (SSLs), primarily inorganic light-emitting diodes [135]. The premise of this brief summary is that the more cost-effective, energy-efficient technology will prevail. However, the enthusiasm for any new technology should be tempered by realities such as the 20-year gestation period for the compact fluorescent lamp to mature and displace even a relatively easy target, the 15 lm W^{−1} incandescent lamp. Based on the properties of plasmas and SSLs, plasma lighting is more competitive when:

- high total lumen output is needed (because metal-halide lamps are already efficient and their cost scales only weakly with lumen output);
- low cost-of-light is key (because fluorescent lighting systems are already efficient and of very low cost, and because most white SSLs have an analogous phosphor downconversion loss); and
- deep ultraviolet radiation is needed (because plasmas can produce radiation from ionized emitting species, while SSLs are limited by the bandgap).

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Plasma modelling at a crossroad

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Status. As a discipline, modelling of low-temperature plasmas (LTPs) has made tremendous advances over the past many years due to improvements in our understanding of the underlying fundamental physics and our ability to represent that understanding in computational algorithms [136]. These developments have been concurrent with vast improvements in access to computational resources. Two-dimensional (and 3D) modelling is now commonly performed for nearly all types of plasmas, from low-pressure discharges for materials processing to atmospheric-pressure plasmas for aeronautical flow control [136]. Modelling is increasingly viewed as a scientific tool on a par with experiments. Although progress has been impressive, there are many phenomena that must still be properly incorporated into models. Doing so collaboratively with fundamental investigations will further both activities.

The Plasma 2010 decadal study by the US National Research Council [137] cites predictability in plasma science and engineering based on fundamental modelling as a requirement for progress in the field. The International Technology Roadmap for Semiconductors [138] cites model-based design for plasma equipment and processes as a necessary capability to achieve the industry's goals. In this sense, there is general agreement on the intellectual and technological importance of modelling of LTPs.

Current and future challenges. In spite of its progress, modelling in LTPs lags behind its counterparts in computational fluid dynamics (CFD) and high temperature and high energy density plasmas (HTEDP) in the sophistication of computational algorithms and adoption of high performance and cloud computing (HPCC) [139]. The reasons are complex, partly due to national priorities and funding, and partly due to the context of the physics being addressed. The wide use of fluid models whose underlying physics does not critically depend on the kinetics of distribution functions has enabled the CFD and HTEDP communities to concentrate more on computational issues. At the same time, there are classes of multiscale and multiphysics problems in LTPs that require HPCC techniques to resolve. To meet these challenges, the LTP community should migrate towards highly parallelized models using advanced techniques such as domain decomposition, unstructured and adaptable meshes, and truly multiscale algorithms [140].

The close alignment of the LTP science community to applications has emphasized the need for performing simulations for industrially relevant chemistries. As a result, there is a continuing need for reaction mechanisms for electron, ion and photon initiated processes in addition to neutral chemistry and plasma-surface reactions [141]. Although LTP science is one of the most challenged of all scientific disciplines in assembling and maintaining these databases and reaction mechanisms, the LTP community also lags behind the combustion and fusion communities which have established archives of such data and mechanisms, and developed funding streams to populate and maintain those databases [142]. Although not the emphasis of this report,

significant progress in LTP modelling cannot be achieved without concurrent advances in the modelling of surface processes. The challenges in surface kinetics modelling parallel those for plasma modelling [143].

The advent and proliferation of commercial plasma modelling (PM) software and broad distribution of university codes has enabled both experts and non-experts in PM to address a broader range of problems. In this sense, the trend is similar to the situation in CFD—less development of unique codes by individuals or teams of researchers and broader use with more tacit acceptance of the validity of commercial or university codes. This tacit acceptance should come with some caution as there are still LTP phenomena that are only approximately treated in many of these codes. The CFD community made this transition to third party codes earlier and in a more deliberate and quantitative manner. Suites of test problems have been established to compare and benchmark codes—the validation-and-verification (V&V) process [144]. To some degree, these are more directly achievable and less ambiguous issues in CFD because the dynamic range of the problems is smaller and the parameter spaces are more easily delineated (e.g. subsonic versus supersonic). Having said that, lack of similar V&V standards in LTPs has hampered progress. Open-source codes work towards these ends by making models widely available whose algorithms and outcomes are transparent to the community.

Advances in science and technology to meet challenges. The two extremes of PM, global modelling (GM) and multi-dimensional modelling (MDM), have served the discipline well. GM enables the development of fundamental understanding and scaling laws, combined with the utility of fast computation. MDM enables detailed examination of plasma transport in specific systems which depends on geometry or is driven by non-uniformities. In those cases where MDM is best used, and in an era where computing resources are seemingly becoming unbounded, there is a tendency to address increased complexity by increasing the size of the problem with more resolution. Although the LTP community should adopt HPCC methods, this field is also unique in serving two distinct but collaborative communities—the science community whose access to HPCC is in principle unlimited and whose time scales are long, and the technology developers whose access to HPCC and time scales are both more limited. It would be optimum to have modelling platforms that serve both communities well. To do so may require hybrid techniques [145] that not only combine different computational techniques but which also combine theory and computations.

There will always be spatial or time scales that are too large or too small to be reasonably addressed computationally yet still need to be resolved. Other disciplines have addressed this dilemma by marrying theory and computations to a greater degree than the LTP community. For example, the CFD community combines theories of microturbulence with large-scale computations to lessen the need for finer resolution. Fundamental theories of plasma kinetics and transport that capture non-equilibrium effects combined with computations

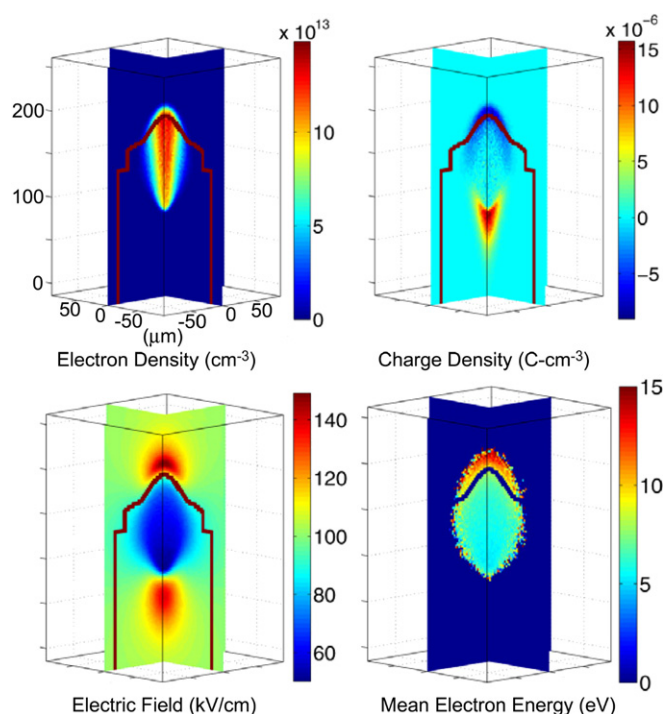


Figure 22. Plasma parameters from a 3D-hybrid simulation for a streamer in air. The lines show the demarcation between regions using a fluid simulation and those using a particle simulation. (Adapted from [145].)

hold the possibility of reducing the scale of the computations while simplifying interpretation of the results. Developing such techniques would serve the broad diversity of the LTP community.

There are also opportunities for innovation in algorithms that rely less on a priori assumptions and allow the dynamics of the system to determine the best computational path forward. For example, self-aware models that automatically choose the optimum computational technique based on local physical parameters (e.g. kinetic transport in regions of non-equilibrium and fluid transport elsewhere) place resources where the most effort is required [145] (see figure 22).

Modelling LTPs has been simultaneously driven by resolving fundamental science issues and by applying that improved modelling capability to technology. New applications will continue to motivate development of new computational techniques which are then leveraged to improve fundamental understanding and design new technologies. Plasmas sustained in and on liquids, plasmas in contact with organic and biological materials, extremely high aspect ratio plasmas (such as through capillary tubes), plasmas

through aerosols and dust clouds, plasmas in high-speed flows, highly intense microplasmas, repetitively pulsed plasmas for control of particle distribution functions, plasmas for material modification and nanostructure fabrication, non-equilibrium kinetics at atmospheric pressure, radiation transport, transport in magnetized systems, and electromagnetic wave phenomena in low-pressure plasmas are examples of where our understanding of the fundamental plasma transport processes can be enhanced through computations. These are also examples for which improving that understanding will rapidly be translated into improvements in technology. Although the emphasis in modelling of LTPs is usually on applications, there is growing interest and importance in the modelling of naturally occurring plasmas, such as sprites [145].

Opportunities also exist to leverage computational V&V techniques developed for plasma modelling in non-LTP areas and to share LTP knowledge with those fields. Direct Simulation Monte Carlo (DSMC) techniques developed for modelling rarefied and hypersonic plasmas, and implicit electromagnetic particle-in-cell (PIC) techniques developed for modelling HTEDP are examples of where knowledge of non-equilibrium kinetics from the LTP community could be leveraged with these advanced computational techniques from other fields. A continuing workshop on V&V for simulations of high-temperature collisional–radiative plasmas could be a model for the LTP community [146].

Concluding remarks. Modelling in LTPs encompasses an intellectually diverse range of activities, from fundamental transport to design of commercial reactors, and now even describing nature's plasmas. The field has made envious progress in developing the fundamental understanding and basic computational techniques that describe many LTPs. The field is, however, at a crossroad. Maintaining this progress may require a community wide change in its mode of operation by borrowing best practices from other disciplines. The marriage of theory and computation, adoption of HPCC techniques, implementing V&V standards or open source codes, and support of community wide databases are examples of practices that have benefited other communities, and could be adopted by the LTP community. However, the LTP community should not measure modelling success by only the number of processors used and the magnitude of the calculation. Success should also be measured by how well modelling has served the science and technology arms of the field with models that address the science but can be broadly implemented to improve technology.

Plasma diagnostics

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Status. The aim of diagnostics is to provide quantitative information on plasma parameters essential for developing an understanding of the processes determining the physics and chemistry in a plasma. In an early phase of an investigation of a novel discharge configuration this might just lead to a basic characterization of the system, while in a more developed phase results need to be combined with models and simulation in order to achieve this goal. However, in industrial application often a less demanding approach is sufficient and only qualitative but sensitive information on the stability or reproducibility of the system is needed for monitoring.

Plasmas are systems with multiple interacting species which are usually distributed rather inhomogeneously. This requires a broad spectrum of different diagnostics with adequate spatial and temporal resolution. Generally, one can distinguish between charged (electrons, positive and negative ions) and neutral species (atoms and molecules). Ideally, distribution functions of the gaseous species are measured but often average values such as densities, fluxes and temperatures are determined. In addition to classical diagnostics in the volume, recent years have shown an increasing interest in *in situ* diagnostics of the interaction of the plasma with the surfaces of substrates, electrodes and the wall. There atoms and molecules experience reactions and the surface structure itself, especially for thin films, is of interest.

The multiple techniques developed over the years can be categorized into optical techniques passively using the emission of the plasma or actively probing the interaction with external radiation, probes of various types immersed into the plasma and sensors that can be integrated into the wall (figure 23). Active optical techniques include various laser and microwave sources as well as lamps or simple diodes. Langmuir, B-dot, thermal, hairpin and other probes are frequently used but care has to be taken about a possible disturbance of the plasma. Mass spectrometers, ion energy analysers and current sensors belong to the category of wall-integrated sensors. In addition, classical current, voltage

and power measurements in the external circuit, including the relative phase and forwarded/reflected power, can provide essential information.

Compared with other fields like surface science, the range of commercially available diagnostics is rather limited and even where diagnostic tools have become available recently, often homemade setups are still frequently found in laboratories. Nevertheless, plasma diagnostics has strongly benefited from recent technical developments like ICCD cameras with up to sub-ns resolution, novel and highly stable lasers, and fast and high resolution micro-electronics for probes, counters and oscilloscopes. This has enabled, for instance, reliable application of various laser techniques such as CRDS, IRLAS or Thomson scattering. A strong focus is now on plasma–surface interaction and a wide spectrum of surface diagnostics such as XPS, ellipsometry, micro-Raman, and others is frequently applied. Last but not least the tremendous development of plasma simulation by modern computers allows now a sensitive in-depth interpretation of measured data that can put diagnostics really on a new level. By comparing measured parameters with the simulation often unmeasured parameters can be extracted from the simulation with some confidence and used for data interpretation. Some useful monographs and recent special issues and reviews can be found in [147–156].

Current and future challenges. At present, non-equilibrium atmospheric-pressure plasmas are experiencing a renaissance in the form of so-called microplasmas. These plasmas have a typical scale length of less than 1 mm and operate often in pulsed or transient modes on time scales of ns or less. The discharge physics can be considerably different due to high collisionality, transient phenomena, and in particular an enhanced influence of plasma–surface interaction. Closely related are discharges in liquids, where the discharge propagates through tiny gas channels and bubbles. Most standard diagnostics established at low pressures in large chambers fail under these conditions, e.g. probes, and others have to be modified, e.g. taking into account strong quenching in LIF. On the other hand certain diagnostics take particular advantage of these conditions, e.g. CARS requires a rather high gas density, and lifetime reduction by quenching strongly enhances the temporal resolution in emission spectroscopy. Nevertheless, many important quantities can still not be determined since the diagnostics are missing. For instance, measuring the ion energy distribution at an electrode in a microplasma is still a challenge. At the same time simulations are also facing new challenges and quantitative experimental results are strongly needed. Clearly, there is a strong need for the development of novel schemes and techniques in order to reach the same standard as at low pressures.

An important motivation for investigating these plasmas is their potential in biomedical applications. This raises new challenges for the *in situ* diagnostics of biological tissues, the parallel monitoring of a number of key radicals produced in the plasma as well as radiation, electric fields and charged particle penetration into the tissue and modifications caused in cells or on their membranes. For classical plasma physics this is an

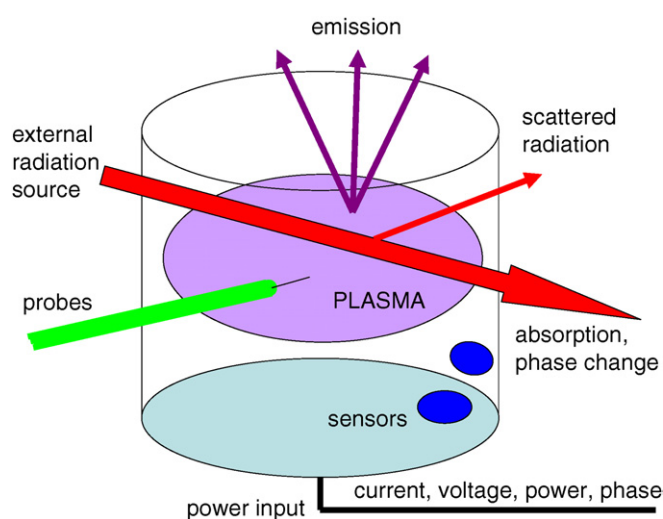


Figure 23. General techniques used to diagnose a plasma.

area as unfamiliar as plasma physics is unknown to biologists and medical doctors. Nevertheless, again there is a strong need for diagnostic development.

For these plasmas as well as low-pressure plasmas, emission spectroscopy has always been one of the major diagnostic methods. The main challenges result from unknown non-Maxwellian velocity distributions, cascading transitions, direct and dissociative excitation channels, and collisional transfer and quenching. The large variety of the various schemes proposed in the literature seems natural with a view on a similar variety of discharge conditions. However, still collisional–radiative models need to be developed further. There is no general answer to the question how to diagnose plasmas optically. In fact, some prior knowledge on the discharge is usually required in order to ensure that a particular scheme is applicable. In any case, a good knowledge of atomic/molecular and plasma physics is required when applying emission techniques. An automated black-box is still not visible on the horizon. However, conditions are more relaxed for monitoring. There indeed for certain applications the plasma emission can serve as a sensitive automated sensor for deviations in the processing conditions.

Surface analysis techniques represent a category of their own and plasma physics has benefited here largely from the recent development in surface science in general. XPS and ellipsometry setups are commercially available and can under some conditions even be integrated *in situ*. Still processes on the surface are often not well known which can be a serious bottleneck, for instance, in the simulation of chemical reactions. Also, elementary parameters such as secondary electron emission and surface recombination coefficients are often unknown and are in fact difficult to determine experimentally.

Finally, many important atomic and molecular cross-sections and rate coefficients are still *terra incognita*. Although here the measurement techniques are generally established they are far from being trivial. Unfortunately, activities on actually carrying out these measurements are rather limited. Programs supporting such efforts would be greatly welcome.

Advances in science and technology to meet challenges. For low-pressure plasmas quite a number of novel probes using microwave frequencies around the plasma frequency

have been developed over recent years such as the hair-pin probe, the plasma absorption probe, the plasma resonance probe and others. The self-excited electron resonance spectroscopy technique detects non-linear current oscillations in the 100 MHz regime. All these probes are already commercialized or have the potential to become a commercial product.

As an alternative to commercial but rather expensive plasma monitor systems (allowing ion energy and mass analysis as well as neutral mass analysis) recently much simpler retarding field analysers have become commercially available. There, no distinction can be made between the mass of the ions but the energy distributions can be determined at low pressures.

In infrared laser absorption spectroscopy, quantum cascade lasers are now often replacing the much more demanding lead-salt systems of the past. In fact, operation can now be very simple and stable so that with a proper computer system fully automated monitoring of certain molecular species is possible. A recent development with high potential is fs THz sources for detection of either molecular species or plasma densities.

Also, intensified CCD cameras have been developed now to a level where stability of the gating, quantum efficiency (especially with GaAs cathodes) and temporal resolution (down to some 100 ps) allows diagnostics not possible in the past. Techniques such as phase-resolved optical emission spectroscopy (PROES) and radio-frequency modulation spectroscopy (RF-MOS) have significantly benefited from this development.

Concluding remarks. As in any field, plasma diagnostics has also taken advantage of recent technical developments. However, a wider availability of commercial diagnostic devices would be highly welcome. The complexity of plasmas requires for their analysis a whole series of different parameters to be determined. The result of a single diagnostic is often ambiguous and ideally a whole spectrum of different diagnostic techniques can be used in parallel. Combination of diagnostics with simulation seems to be one of the most powerful directions for the future. In any case, carrying out plasma diagnostics requires a very detailed understanding of the physics and care has to be taken not to be misguided by artefacts.

Atomic and molecular data for plasma physics—challenges and opportunities

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Status. Control of plasma processing methodologies can only occur by obtaining a thorough understanding of the physical and chemical properties of plasmas [157, 158]. However, all plasma processes are currently used in the industry with an incomplete understanding of the coupled chemical and physical properties of the plasma involved. Thus, they are often ‘non-predictive’ and hence it is not possible to alter the manufacturing process without the risk of considerable product loss. Indeed, a US National Research Council Board report on plasma processing [159] stated that ‘plasma process control remains largely rudimentary and is performed predominantly by trial and error’, an expensive procedure which limits growth and innovation of the industry.’ The same report therefore concluded that ‘A clear research imperative in the next decade will therefore be to increase our knowledge of the chemical and physical interactions in such plasmas of electrons, ions and radicals with neutral species’. Although written more than a decade ago these comments are still valid and only a more comprehensive understanding of such processes will allow models of such plasmas to be constructed that in turn can be used to design the next generation of plasma reactors.

Developing such models and gaining a detailed understanding of the physical and chemical mechanisms within plasma systems is intricately linked to our knowledge of the key interactions within the plasma and thus the status of the database for characterizing electron, ion and photon interactions with those atomic and molecular species within the plasma and knowledge of both the cross-sections and reaction rates for such collisions, both in the gaseous phase and on the surfaces of the plasma reactor.

The compilation of databases required for understanding most plasmas remains inadequate. The spectroscopic database required for monitoring both technological and fusion plasmas and thence deriving fundamental quantities such as chemical composition, neutral, electron and ion temperatures is incomplete with several gaps in our knowledge of many molecular spectra, particularly for radicals and excited (vibrational and electronic) species. Similarly, complete and consistent datasets for electron scattering cross-sections from most molecular species encountered in commercial plasmas are limited to only a few systems (water, oxygen and nitrogen), and even these compilations remain the subject of debate; indeed, for many important molecules used in industry (e.g. fluorocarbons for etching) such data has never been compiled. A similar narrative holds for ion and neutral molecule reactions with the additional proviso that when data are available the rate constants are usually at room temperature, whereas they are often required at elevated temperatures. The situation is even worse when considering atmospheric plasmas [160] where many of the ions and some neutrals are in clusters for which we know few cross-sections/reaction rates or even spectroscopic signatures. ‘Finally’ all plasmas are confined hence wall interactions are important, indeed such reactions often dominate the physics and plasma chemistry

requiring sticking coefficients and cross-sections/reaction rates on surfaces [161, 162]—but to date these are unknown and even how they should be defined remains subject to debate.

Given the preceding discussion it may appear that it has proven impossible to model/interpret any plasma system, however, this is far from the case. Our knowledge of atomic spectroscopy and collisions is good with theoretical techniques able to provide reliable data where experimental measurements are missing or not practical (e.g. for C targets which cannot be prepared in the laboratory). Recent models of He and Ar plasmas have been found to agree well with diagnostic observations [157, 163]. Similarly atmospheric (N_2 and O_2) and many fluorocarbon-containing plasmas have been modelled using a mixture of experimental and theoretical data providing a satisfactory representation of the consequences of plasma application (e.g. etch rates and profiles) but they are still far from being predictive and no commercial industry has based the design of their fabrication reactors on models alone [164, 165].

Current and future challenges. The atomic and molecular community recognizes the major needs of the applied communities and over the past decade has developed novel and sophisticated tools to study spectroscopic and collisional parameters with an increasing range of targets, including radicals. For example, they have developed cavity ring down spectroscopy, velocity mapping and coldtrims to ‘image’ electron and ion collisions and adopted surface science methods to study atoms and molecules on surfaces including the use of STM.

However, the compilation of fundamental atomic and molecular data required for such plasma databases is rarely a coherent, planned research programme, instead it is a parasitic process. In fact, today it is rare for atomic and molecular physics researchers to be funded to measure fundamental spectroscopy or collision processes since these are no longer regarded in themselves as ‘cutting edge’ research, rather, the field has developed to explore more exotic phenomena such as cold atoms, nanotechnology and chemical control. Thus, the greatest challenge to the atomic and molecular community is to maintain the infrastructure (including people) that will allow the fundamental data to be collected. This in turn challenges the wider scientific community to recognize that their fields rely upon such data. A united applied and fundamental research community must then confront the funders of research (government and industrial) and specify that scientific and technological progress is based upon a strong fundamental bedrock and that if this is neglected then the scientific and technological advances they require will not occur and their investment will not be rewarded.

More immediately, the plasma community must identify its key needs to the atomic and molecular physics community which must in turn present the plasma community with a more coherent, commonly approved set of databases. Databases listing atomic and molecular data have been assembled for over 40 years, initially purely in print form and often as lengthy reviews—indeed there are journals that have specialized in such data compilations (*The Journal of Chemical Physics*

Reference Data). Some of these databases have acquired international status being widely accessed by the international community, for example the AMBDAS and ALADDIN databases compiled by the Atomic and Molecular (A&M) Data Unit as part of the Nuclear Data Section of the International Atomic Energy Agency, Vienna, Austria. However, to date these databases (databanks) have acted independently of one another providing the user with a myriad of conflicting recommendations. The scientific community must therefore address this issue to formulate an international network of data standards. For example, A&M data will be essential in the ITER reactor which will contain diagnostic tools developed by different international teams; such tools cannot be calibrated using different sets of cross-sections as listed in different national databases.

Advances in science and technology to meet challenges. The fundamental research community, the providers of such data, needs to assemble, update and police a set of approved databases. This is no longer as complicated as it was a decade ago. Most publications are accessible online and most authors place their data on home pages and in archives. Hence compiling databases is easier than it was in the past, for example by using the **General Internet Search Engine** for Atomic Data (GENIE) developed as part of the International Atomic Energy Agency facility for collisional atomic data for fusion and atomic physics research [166]. In the future such electronic databases will provide the opportunity for authors to both add results to the database and provide a forum for discussing such data. Such procedures should allow future databases to be constructed more easily, be maintained more regularly and be accessed more commonly by users who may be confident of the standards and accuracy of the data provided. The EU supported Virtual Atomic and Molecular Data Centre (VAMDC) is being developed with this philosophy aiming to provide a 'one stop' data resource that will support researchers across a wide range of fields, including the plasma community [167, 168] by allowing access to more than 20 databases through a single portal. In the future this architecture

can be extended to include all of the major international A&M databases and provide a forum for standardizing datasets.

As stated above, the experimental community is developing novel techniques that have the potential to meet many of the challenges and data needs of the plasma community, but even if adequately supported financially the experimental community can never compile the amount and variety of data the plasma community needs and should therefore be increasingly used to 'benchmark' theoretical formalisms that can mass produce the data needed by users. In fact this is already true in spectroscopy where the millions of transitions needed for astronomy and aeronomy are generated by computational codes validated against a selected set of high-accuracy measurements. It should therefore be a goal to add to such databases access to theoretical tools that will allow the user to evaluate cross-sections for targets and scattering processes for which experimental data are not yet available. Indeed there already exist several methods for evaluating electron impact ionization cross-sections while some commercial software evaluates a wide range of cross-sections.

Conclusions. The plasma community is a rapacious user of atomic and molecular data but is increasingly faced with a deficit of data necessary to both interpret observations and build models that can be used to develop the next-generation plasma tools that will continue the scientific and technological progress of the late 20th and early 21st century. It is therefore necessary to both compile and curate the A&M data we do have and thence identify missing data needed by the plasma community (and other user communities). Such data may then be acquired using a mixture of benchmarking experiments and theoretical formalisms. However, equally important is the need for the scientific/technological community to recognize the need to support the value of such databases and the underlying fundamental A&M that populates them. This must be conveyed to funders who are currently attracted to more apparent high-profile projects.

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