Lecture 1

The Major Component of the Universe, the Cornerstone of Microelectronics, The High-Tech Magic Wand of Technology

1.1 The Forth State of Matter: Plasma in Nature, in Lab, in Technology

Walking the streets of a beautiful city of Belgrade with an excellent plasma scientist and friend Zoran Petrovic, I have been shocked by and took pictures of the huge billboards claiming “Plasma, that’s all you need,” see Figure 1.1. When asking people on the streets of the Serbian capital: “Why all you need is plasma?”, the best answer was “because… plasma is good!”. Surely, they meant their popular brand of tasty soft biscuits, but still, I agree with them: plasma is good! Before asking ourselves what’s so good about plasma, let’s introduce the term plasma, which means for us neither the Serbian cookies nor component of blood, but the very special fourth state of matter.

Plasma is an ionized gas, a distinct fourth state of matter. “Ionized” means that at least one electron is not bound to an atom or molecule, converting the atoms or molecules into positively charged ions. As temperature increases, molecules become more energetic and transform matter in the sequence: solid, liquid, gas, and finally plasma, which justifies the title **“fourth state of matter.”** The free electric charges, electrons, and ions, make plasma electrically conductive, sometimes more than gold and copper, internally interactive, and strongly responsive to electromagnetic fields. *The ionized gas is called plasma when it is electrically neutral (i.e. electron density is balanced by that of positive ions) and contains a sufficiently high number of the electrically charged particles to affect its electrical properties and behavior*. In addition to being important in many aspects of our daily lives, *plasmas are estimated to constitute more than 99% of the visible universe*.

The term plasma was first introduced by Irving Langmuir in 1928. The multicomponent, strongly interacting ionized gas reminded him of blood plasma (thus at least no direct connection with the tasty soft biscuits). Langmuir wrote: “Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name plasma to describe this region containing balanced charges of ions and electrons.” There is usually not much confusion between the fourth state of matter (plasma) and blood plasma; probably the only exception is the process of plasma-assisted blood coagulation, where the two concepts meet.

Plasmas occur naturally but also can be effectively man-made in laboratory and in industry, which provides opportunities for numerous applications, including thermonuclear synthesis, electronics, lasers, fluorescent lamps, and many others. To be more specific, most computer and cell phone hardware is made based on plasma technologies, not to forget about plasma TV. Plasma offers three major attractive features: (i) temperatures of at least some plasma components and energy density can significantly exceed those in conventional technologies, (ii) plasmas can produce very high concentrations of energetic and chemically active species (e.g. electrons, ions, atoms and radicals, excited states, and different wavelength photons), and (iii) plasma systems can essentially be far from thermodynamic equilibrium, providing extremely high density of active species keeping bulk temperature as low as room temperature.

These plasma features permit intensification of conventional chemical processes, increases their efficiency, and often even permit reactions impossible in conventional chemistry. Plasma today is a rapidly expanding area of science and engineering, with technological applications widely spread from micro-fabrication in electronics to making protective coatings for aircrafts, from treatment of polymer fibers and films before painting to medical cauterization for stopping blood and wound healing, from food safety to treatment of cancer, and from production of ozone to the plasma TVs. Summarizing, “plasma is good.”

Plasma Science and Technology: Lectures in Physics, Chemistry, Biology, and Engineering, First Edition. Alexander Fridman.

Figure 1.1 "Plasma, that's all you need," how about that?!

Plasma comprises most of the universe: the solar corona, solar wind, nebula, and Earth's ionosphere are all plasmas. Lightning is the plasma phenomenon in Earth's atmosphere, well observed and used by humans from their early days. The breakthrough experiments with this natural form of plasma were performed long ago by Benjamin Franklin, which probably explains the special interest to plasma research in Philadelphia, where the author of this book works at the Nyheim Plasma Institute of Drexel University. At altitudes of approximately 100 km, the atmosphere no longer remains nonconducting due to ionization and formation of plasma by solar radiation. As one progresses further into near-space altitudes, the Earth's magnetic field interacts with charged particles streaming from the sun. These particles are diverted and often become trapped by the Earth's magnetic field. The trapped particles are most dense near the poles and account for the aurora borealis. **Lightning and the aurora borealis** are the most common natural plasmas observed on Earth.

Natural and man-made plasmas (generated in gas discharges) occur over a wide range of pressures, electron temperatures, and electron densities, see Figure 1.2. The temperatures of man-made plasmas range from slightly above room temperature to temperatures comparable to the interior of stars, and electron densities span over 15 orders of magnitude. Most plasmas of practical significance, however, have electron temperatures of 1–20 eV, with electron densities in the range 10^6–10^{18} cm^{-3}. *The high temperatures are conventionally expressed in electron volts; 1 eV approximately equals 11 600 K*. Not all particles need to be ionized in plasma, a common condition is for the gases to be only partially ionized. The ionization degree (i.e. ratio of density of major charged species to that of neutral gas) in the conventional plasma engineering systems is in the range 10^{-7}–10^{-4}. When the ionization degree is close to unity, such plasma is called **completely ionized plasma**. Completely ionized plasmas are conventional for thermonuclear plasma systems: tokamaks, stellarators, plasma pinches, focuses, and so on. When the ionization degree is low, the plasma is called **weakly ionized plasma**, which is the focus of most of this book. Both natural and

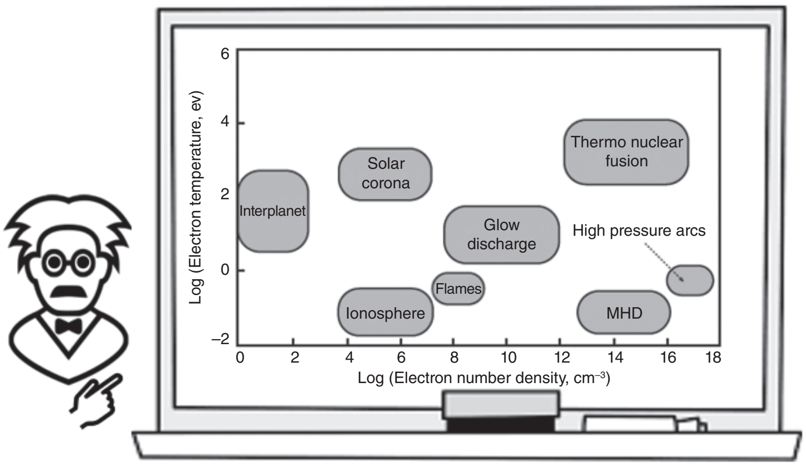


Figure 1.2 Electron temperatures and number densities in different plasmas.

man-made laboratory plasmas are quasi-neutral, which means that concentrations of positively charged particles (positive ions) and negatively charged particles (electrons and negative ions) are well balanced. Langmuir was one of the pioneers who studied gas discharges and defined plasma to be a region not influenced by its boundaries. The transition zone between the plasma and its boundaries was termed the **plasma sheath**. The properties of the sheath differ from those of the plasma, and these boundaries influence the motion of the charged particles in this sheath. The particles form an electrical screen for the plasma from influences of the boundary.

1.2 Multiple Plasma Temperatures, Plasma Nonequilibrium, Thermal and Nonthermal Plasmas

Temperature in plasma is determined by the average energies of the plasma particles (neutral and charged) and their relevant degrees of freedom (translational, rotational, vibrational, and those related to electronic excitation). Thus, plasmas, as multi-component systems, can exhibit **multiple plasma temperatures**. In the electric discharges common for plasma generation in the laboratory, energy from the electric field is first accumulated by the electrons between collisions and, subsequently, is transferred from the electrons to the heavy particles. Electrons receive energy from the electric field during their mean free path and, during the following collision with a heavy particle, lose only a small portion of that energy (because electrons are much lighter than the heavy particles). That is why *the electron energy and temperature in plasma can be higher than those of heavy particles. Subsequently, collisions of electrons with heavy particles (Joule heating) can equilibrate their temperatures. This "equilibration" doesn't happen if time or energy are not sufficient (which occurs, for example, in coronas and pulsed discharges) or if there is an intensive cooling preventing heating of the entire gas (which occurs, for example, in wall-cooled low-pressure discharges). This determines the* ***basic plasma nonequilibrium*** *($T_e \gg T_0$).* The temperature difference between electrons and heavy neutral particles due to Joule heating in the collisional weakly ionized plasma is usually proportional to the square of the ratio of electric field (E) to pressure (p). Only in the case of low E/p, the temperatures of electrons and heavy particles approach each other. This is a basic requirement for **local thermodynamic equilibrium (LTE)**. The LTE conditions also require chemical equilibrium and restrictions on gradients. The *LTE plasma follows the major laws of equilibrium thermodynamics and can be characterized by a single temperature at each point of space. Ionization and chemical processes in such plasmas are determined by a single temperature (and only indirectly by E/p through Joule heating)*. The quasi-equilibrium plasmas of this kind are usually called **thermal plasmas**. Thermal plasmas in nature are represented by solar plasma and lightning.

Numerous plasmas exist very far from the thermodynamic equilibrium and are characterized by multiple different temperatures related to different plasma particles and different degrees of freedom. It is the electron temperature that often significantly exceeds that of heavy particles ($T_e \gg T_0$). Ionization and chemical processes in such **nonequilibrium plasmas** are directly determined by electron temperature and, therefore, are not so sensitive to thermal processes and temperature of the gas. The nonequilibrium plasma of this kind is called **nonthermal plasma**. An example of nonthermal plasmas in nature is the aurora borealis. Although the relationship between different plasma temperatures in nonthermal plasmas can be quite sophisticated, it can be conventionally presented in the collisional weakly ionized plasmas as $T_e > T_v > T_r \approx T_i \approx T_0$. Electron temperature ($T_e$) is the highest in the system, followed by the temperature of vibrational excitation of molecules (T_v). The lowest temperature is usually shared by heavy neutrals (T_0), temperature of translational degrees of freedom or simply gas temperature), ions (T_i), as well as rotational degrees of freedom of molecules (T_r).

In many **nonthermal plasmas**, electron temperature is about 1 eV (about 10 000 K), whereas the gas temperature is close to room temperature. Nonthermal plasmas are usually generated either at low pressures or at lower power levels, or in different kinds of pulsed discharge systems. The engineering aspects and application areas are quite different for thermal and nonthermal plasmas. For example, thermal plasmas are usually more powerful, whereas nonthermal plasmas are more chemically selective.

It is interesting to note *that both thermal and nonthermal plasmas usually have the highest temperature (T_e in one case, and T_0 in the other) on the order of 1 eV, which is about 10% of the total energy required for ionization (ionization potential, about 10 eV). It reflects the general rule found by Zeldovich and Frank-Kamenetsky for atoms and small molecules in chemical kinetics: the temperature required for a chemical process (including ionization) is typically about 10% of the total required energy, which is the Arrhenius activation energy* *(or ionization potential in plasma)*. Funny, a similar **rule of 10%** can usually be applied to determine a down payment to buy a house or a new car. Thus, the plasma temperatures can be somewhat identified as the "down payment for the ionization process." Thus, in the thermal quasi-equilibrium plasmas, the single temperature is about 1 eV. In the strongly nonequilibrium nonthermal plasmas, the electron temperature is on the order of 1 eV, while gas temperature can be from the room temperature and above simply following the heating/cooling balance.

1.3 Plasma Sources: Nonthermal, Thermal, and Transitional "Warm" Discharges, Discharges in Gases and Liquids

Plasma sources, which in most of practical cases are the electric discharges, represent the engineering basis of the plasma science and technology. For simplicity, an electric discharge can be first viewed as two electrodes inserted into a tube and connected to a power supply. It was Michel Faraday, who was observing and investigating such plasma sources as early as in 1830s. The tube can be filled with various gases or evacuated. As the voltage applied across the two electrodes increases, the current suddenly increases sharply at a certain voltage required for sufficiently intensive electron avalanches. If the pressure is low, on the order of a few Torrs, and the external circuit has a large resistance to prohibit a large current, a **glow discharge** develops. This is a low-current, high voltage discharge widely used to generate nonthermal plasma with T_e about 1 eV and above, and T_0 about room temperature. A similar discharge is known to everyone as the plasma source in fluorescent lamps (you can touch it to double-check that T_0 is about room temperature). *For educational purposes, the glow discharge can be considered as a major example of low-pressure nonthermal plasma sources*, see Figure 10.1 in Lecture 10.

A nonthermal **corona discharge** occurs at high pressures (including atmospheric pressure) only in regions of sharply nonuniform electric fields. Glowing powerlines and spikes on top of high buildings are examples of the coronas, which originated the name of the discharges meaning "crowns" in several languages. The electric field near one or both electrodes of the corona discharges must be stronger than in the rest of the gas. This occurs near sharp points, edges, or small-diameter wires. These discharges tend to be low-power plasma sources limited by the onset of electrical breakdown of the gas. It is possible, however, to circumvent this restriction using short-pulse power supplies and organizing large-scale arrays of the more powerful **pulsed coronas**. Figure 1.3 shows example of the 10-kW pulsed corona. The picture is made through a window of the Mobile Environmental Laboratory, see Figure 24.5 in the Lecture 24. Electron temperature in the corona discharges exceeds 1 eV, whereas the gas remains at room temperature. The corona discharges are widely applied in the treatment of polymer materials: most synthetic fabrics applied to make clothing have been treated before dying in corona-like discharges to provide sufficient adhesion. *For educational purposes, the corona discharges can be considered as major example of atmospheric pressure nonthermal plasma sources*, see Figures 13.2 and 13.3 in Lecture 13.

If the pressure is high, on the order of an atmosphere, and the external circuit resistance is low, an **electric arc discharge** can be organized between two electrodes. This discharge is also one of the longtimers, it has been invented

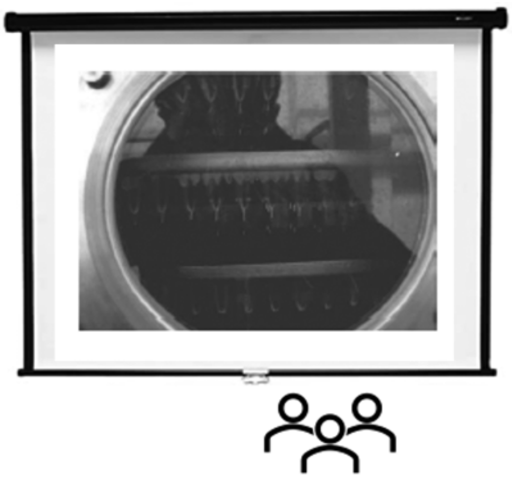


Figure 1.3 Photo of the 10-kW pulsed corona discharge through a window of the Mobile Environmental Laboratory.

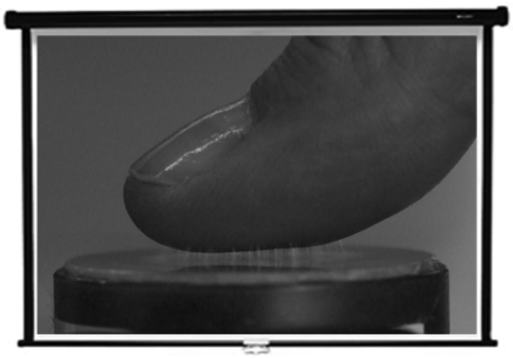
by Sir Humphry Davy in 1800. Thermal arcs usually carry large currents, greater than 1 A at voltages of the order of tens of volts. Furthermore, they release large amounts of thermal energy at very high temperatures often exceeding 10 000 K. The arcs are often coupled with a gas flow to form high-temperature plasma jets. The arc discharges are well known not only to scientists and engineers but also to the public because of their wide applications in welding devices. *For educational purposes, the arc discharge can be considered a major example of thermal plasma sources*, see Figure 11.2 in Lecture 11.

Between other electric discharges widely applied in plasma science and technology, we can point out the **nonequilibrium, low-pressure radiofrequency discharges** playing the key roles in sophisticated etching and deposition processes of modern micro-electronics, micro-electro-mechanics, as well as in treatment of polymer materials, see Figure 12.7 in Lecture 12. It is these discharges manufacture for us most our cellphones or computers, which we are enjoying so much. Between less traditional but very practically interesting discharges, we can point out the nonthermal, high-voltage, atmospheric-pressure, **floating-electrode dielectric barrier discharge (FE-DBD)**, which can use the human body as a second electrode without damaging the living tissue. Such discharge obviously provides very interesting opportunities for direct plasma applications in biology and medicine, see Figure 1.4. FE-DBDs are younger members of the big family of the dielectric barrier discharges (DBD), introduced as early as 1857 by Werner von Siemens, and playing an important role in generation of ozone, plasma TVs, plasma aerodynamics, plasma medicine, and agriculture, see Figures 13.5 and 13.6.

As it was explained above in the Section 1.2, *electron temperature in most of plasma systems stay on the level of 10 000 K (about 1 eV, which is 10% of the ionization potential). Gas temperature controlled by the gas heat balance can be close to room temperature (nonthermal plasma) or vice versa close to electron temperature (thermal plasma). Although plasma is often goes to these extremes, it can be also organized in the intermediate regime of the so-called* ***transitional or warm plasmas****, where T_e is still around 1 eV, but gas temperature can be "warm", around 1000 K and below*. Members of this group include **microwave discharges, sparks** (see the transitional PHD spark discharge in Figure 1.5), as well as different types of the **gliding arc discharges**. The most known recently are the gliding arc discharges stabilized in reverse vortex "tornado" flow generating high power nonequilibrium atmospheric pressure plasma, see Figure 1.6. These discharges provide a unique opportunity of combining the high power and atmospheric pressure typical for arc discharges with the relatively high level of nonequilibrium and therefore selectivity typical for nonthermal discharges.

While majority of electric discharges generate plasma in gas phase, some discharges are operating effectively to generate **plasma in liquid phase**. Most of them like gliding arcs and sparks generate plasma in bubbles or voids in the liquid, see Figure 1.7. These types of "liquid discharges" are applied for chemical and biological cleaning of water, as well as for medical, agricultural, and food processing purposes. Some plasma sources, usually based on the nano-second and sub-nanosecond-based high-voltage pulsing with extremely short voltage rise time, are able, however, directly ionize liquids without bubbles and voids. *So, plasma is not necessarily only "ionized gas," but it can be also "directly ionized liquid."* All these plasma sources, and many others are going to be considered in the Part 2 of this book, Lectures 9–16.

Figure 1.4 Floating-electrode dielectric barrier discharge, FE-DBD.



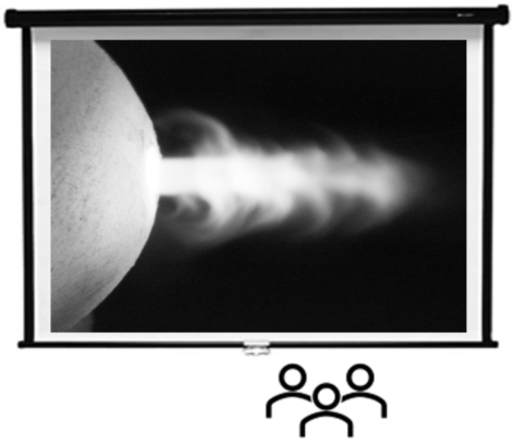


Figure 1.5 Pin-to-hole (PHD) spark discharge.

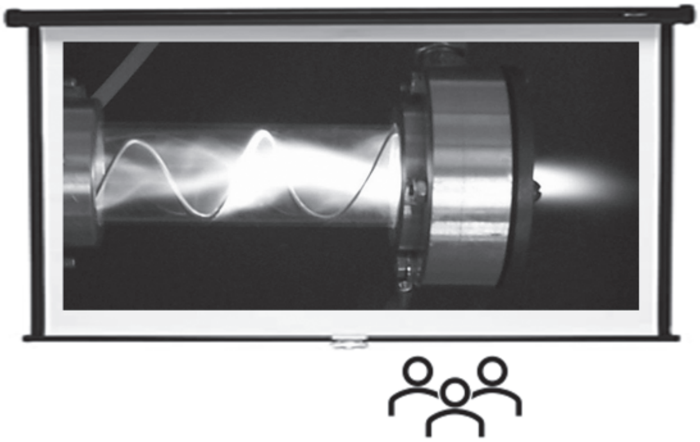


Figure 1.6 Gliding arc discharge stabilized in reverse-vortex “tornado” flow.

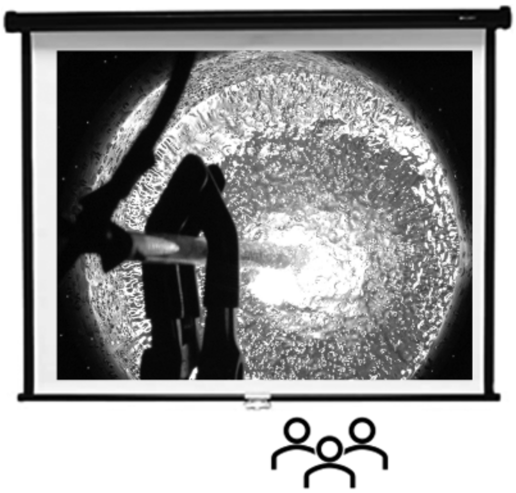


Figure 1.7 Spark discharge in water.

1.4 Plasma Processes: Major Plasma Components, High Selectivity and Controllability of Nonequilibrium Reactions, "Multidisciplinarity Without Borders"

Chemically and biologically active plasmas are multi-component systems highly reactive due to large concentrations of charged particles (electrons, negative and positive ions), excited atoms and molecules (electronic and vibrational excitation make a major contribution), active atoms and radicals, and ultraviolet (UV) photons. In thermal plasmas, the main global effect is mostly due to temperature and relevant quasi-equilibrium plasma components. In nonthermal nonequilibrium plasma, the processes are way more sophisticated. Each component of the chemically active plasma plays its own specific role in plasma-chemical kinetics. The **plasma electrons**, for example, are usually first to receive the energy from an electric field and then distribute it between other plasma components and specific degrees of freedom of the system. *Changing parameters of the electron gas (density, temperature, electron energy distribution function) often permit control and optimization of plasma-chemical processes.*

The **plasma ions** are charged heavy particles, that can make a significant contribution to plasma-chemical kinetics either due to their high energy (as in the case of sputtering and reactive ion etching) or due to their ability to suppress activation barriers of chemical reactions. This second feature of the plasma ions results in the so-called **ion or plasma catalysis**, which is particularly important in the plasma-assisted ignition and flame stabilization, fuel conversion, hydrogen production, exhaust gas cleaning, and even in plasma medicine and agriculture due to the direct plasma-catalytic treatment of living tissue. The energetic plasma ions also significantly contribute to the **reactive ion etching processes** crucial in the microelectronics for the deep ditch anisotropic etching and fabrication of the sophisticated relevant features in the integrated circuits.

The **vibrational excitation of molecules in plasma** often makes a major contribution to the plasma-chemical kinetics and energy balance because the plasma electrons with energies around 1 eV primarily transfer most of their energy in such gases as N_2, CO, CO_2, H_2, CH_4 and so forth into vibrational excitation. The vibrational excitation of molecules is also the most effective in overcoming the activation barriers of the endothermic chemical reactions. Stimulation of plasma-chemical processes through vibrational excitation permits the highest values of energy efficiency to be reached, which occurs for example in the plasma-chemical dissociation of CO_2, and plasma synthesis of NO in air.

Electronic excitation of atoms and molecules in plasma can also play a significant role in plasma kinetics, especially when the lifetime of these excited particles is quite long (as in the case of metastable electronically excited atoms and molecules). As an example, we can mention plasma-generated **metastable low-energy electronically excited oxygen** molecules $O_2(^1\Delta_g)$, singlet oxygen, which effectively participate in the plasma-stimulated oxidation process in polymer processing, and biological and medical applications of plasma. The singlet oxygen $O_2(^1\Delta_g)$ metastable molecules have very long radiative lifetime, about an hour. As an example of the **higher energy metastable electronically excited states of molecules** generated in plasma, we can mention those of nitrogen $N_2\left(A^3\Sigma_u^+\right)$ characterized with radiative lifetime of 13 s and playing significant role, for example, in ozone synthesis in air and plasma-assisted combustion and flame stabilization. In both applications, these quite energetic metastable nitrogen molecules (energy exceeding 6 eV) are able directly dissociate O_2 molecules producing oxygen atoms. Also, they can dissociate the passive radicals HO_2 to suppress the chain termination of oxidation of H_2 and hydrocarbons crucial for plasma-stimulated ignition, combustion, and flame stabilization.

The contribution of the **plasma-generated active atoms and radicals** is obviously also very significant. As an example, we can point out that O atoms and OH radicals effectively generated in atmospheric air discharges which play a key role in numerous plasma-stimulated oxidation processes. They are part of the family of the so-called **reactive oxygen species (ROS)**, which together with **reactive nitrogen species RNS** (like NO, peroxynitrite, nitrosylated organics, etc.) are the key players in the plasma-stimulated biochemistry especially in the liquid phase. F-atoms and the fluorocarbon radicals generated in low-pressure plasmas in C_2F_6, C_3F_8, NF_3, etc. play an important role in etching and other material processing reactions in microelectronics. We should mention that relatively stable long-living active chemicals like ozone, H_2O_2, NO_x compounds, and acids are also crucial in several plasma-initiated chemical and biochemical processes. **Plasma-generated photons** play a key role in a wide range of applications, from plasma light sources to UV sterilization of water. Sometimes strong plasma effects are due to **plasma-related**

electric fields like in the case of plasma-stimulated electroporation of cells so much important in plasma medicine and agriculture.

Plasma is not only a multi-component system, but often a **strongly nonequilibrium system**, like it was already discussed above in the Section 1.3. Concentrations of the active species described earlier can exceed those of quasi-equilibrium systems by many orders of magnitude at the same gas temperature. Also, these *nonequilibrium concentrations of active species are very sensitive to electric discharge and plasma parameters, like electric fields, currents, energy input, composition, etc. It opens possibility of very flexible control of the plasma processes from plasma microelectronics to plasma treatment of cancer. The high level of* ***controllability of the nonequilibrium reactions*** *in plasma permits achievement of very* ***high selectivity of the plasma processes***.

The successful control of plasma permits chemical and biochemical processes to be directed in a desired direction, selectively, and through optimal desired mechanism. Thus, plasma at different regimes can effectively produce NO in air for production of fertilizers and explosives and effectively destroy it in air for the environmental control purposes. Plasmas at different regimes can heal human tissue for treatment of chronic wounds and can selectively destroy the tissue to cancer treatment and for tissue ablation purposes. Surely, plasma is simply a tool but with very high level of controllability and selectivity. A hammer and a computer are also tools: hammer is an excellent tool but focused on one specific application to hit something, while computers are way more controllable and can be used for very many purposes from checking e-mails, participating in ZOOM meetings, and watching movies to writing books, and even hitting something if necessary. Thus, plasma as a tool due to its high controllability and selectivity is way closer to computers from this perspective. Surely effective control of the plasma systems requires detailed understanding of physics, chemistry, if necessary, biology, and surely engineering of the plasma processes. It makes plasma "multidisciplinary without borders" and creates challenge for scientists and engineers working with the "fourth state of matter". Meeting this challenge of the **"multidisciplinarity without borders"** is probably the major objective of this book of lectures.

1.5 Plasma Technologies: The Cornerstone of Microelectronics, the Major Successes Stories

The plasma technologies today are numerous and involve many industries. Discussion of all major plasma applications covers the whole second half of this book (Lectures 17–32). Between those, we can clearly point out the **plasma application to processing of electronic materials**, which can be proudly called the cornerstone of modern microelectronics. Plasma etching, especially deep ditch etching, sputtering, plasma-enhanced chemical vapor deposition (PE-CVD), ion implantation processes, etc. (see Lecture 21), today these plasma technologies determine the success of modern microelectronics, the so wide use of computers, cell phones, and entire almost infinite family of electronic devices, which represent our today's civilization. Just this one plasma application would be sufficient to justify importance of plasma science and technology to modern mankind. There are, however, several other significant plasma success stories.

In this regard, we can point out the **plasma technologies of production and spraying of powders**, and deposition of special coatings. These thermal plasma technologies are usually focused on the protective and specially functionalized coatings. Majority of the parts constituting modern aerospace and automotive engines, construction parts, and other elements undergoing today's thermal spraying for special coatings, significant percentage of those are plasma-related (see Lecture 20). This is today, probably, the number one industrial application of the thermal plasma systems. The thermal plasma spraying, and coating systems can be quite big, like the Drexel vacuum arc coating chamber built by Prof. R. Knight and his team shown in Figure 1.8. Between other successful **large-scale applications of thermal plasma**, we can mention conversion of natural gas to acetylene and ethylene, different ignition schemes, commutation devices, UV sources, plasma metallurgy, and plasma cutting, as well as plasma-stimulated treatment of waste, especially municipal waste, and radioactive waste.

The most successful large-scale applications of nonthermal plasma, outside of electronics, is **plasma treatment of synthetic fibers, fabrics, films,** etc., see Lecture 26. Most of these synthetic materials are plasma treated today to increase adhesion before printing, dying, etc. The very large-scale nonthermal plasma technology is **plasma generation of ozone**, see Lecture 18. The old but impressive photo of the large-scale ozone generator at the Los

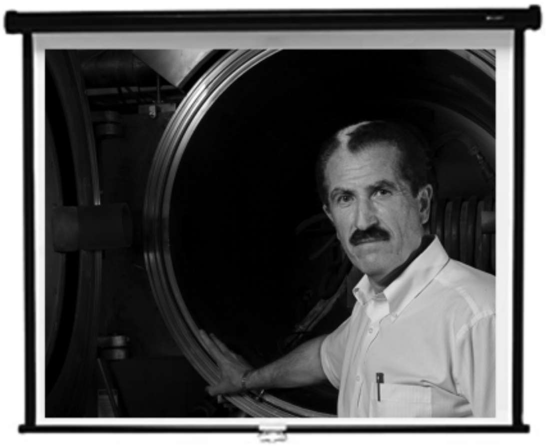


Figure 1.8 Drexel vacuum arc plasma coating chamber.

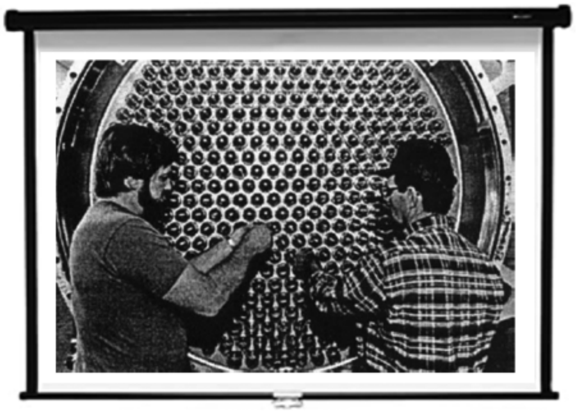


Figure 1.9 Large scale industrial ozone generator.

Angeles Aqueduct Filtration Plant is shown in Figure 1.9. Plasma-generated ozone is widely used in the world for water cleaning. Another plasma-based environmental technology is **plasma cleaning of air and exhaust gases**, industrially applied now in quite large scale in power plants (abatement of NO_x) and automotive tunnels (abatement of automotive exhaust), small units are used to suppress the automotive exhaust inside of cars and trucks, see Lecture 24. First impressive steps are made in **plasma cleaning and disinfection of water**. Not to forget is the large-scale commercial application of nonthermal plasma in different kind of **light sources** from common fluorescent lamps to plasma TVs and plasma-based lasers, see Lecture 23. As a reminder, less than 20 years ago, the incandescent light bulbs dominated the lighting sections of our supermarkets, and now it is very difficult even to find them in the store. The mass-market lighting is now almost completely based on plasma and light-emitting diodes (LED).

Exciting novel application of plasma is **plasma medicine**, that is direct application of plasma to human body to treat diseases, see Lectures 30–32. Largely started only in 2003, it came now to hospitals to treat diseases not effectively treated before. The best results are demonstrated so far in treatment of chronic wounds, especially ulcers, as well as in dermatology. First impressive results are demonstrated in oncological hospitals, in treatment of cancer. Promising results are demonstrated in clinical dermatology, first interesting research data collected in dentistry, gastroenterology, and ophthalmology, see illustration of the animal studies in ophthalmology in Figure 1.10. We should mention, that although the nonthermal plasma medicine itself is a relatively newcomer to the hospitals, the thermal

Figure 1.10 Plasma ophthalmology, animal studies.

plasma-based **blood cauterization technology** is widely used in hospitals already for many decades. Also, plasma technologies have relatively long success story in the thermal **plasma-induced tissue ablation**, as well as in non-thermal plasma-induced **tissue engineering** and sterilization of **medical devices**.

Closely related to the plasma medicine are first impressive technological results in **plasma agriculture and food processing** (Lecture 29), see illustration in Figure 1.11, Plasma has been demonstrated as a reliable tool to treat fresh produce and other foods increasing their shelf life and suppressing dangerous pathogens. Plasma, especially the dielectric barrier discharges, DBDs, has also proven to be effective in disinfection of already packaged food. No miracles, these discharges operate always through dielectric barriers, and the packaging material is just an additional barrier (if it is surely not conductive). The plasma agriculture and food processing technologies are organized not only directly but also through plasma activation of water to stimulate plant growth (especially in hydroponics) and to wash the fresh produce. Talking about plasma technologies, we should at least mention the nuclear fusion. This is a "big one" requiring special consideration of the relevant science and technology but stays outside of the scope of this book.

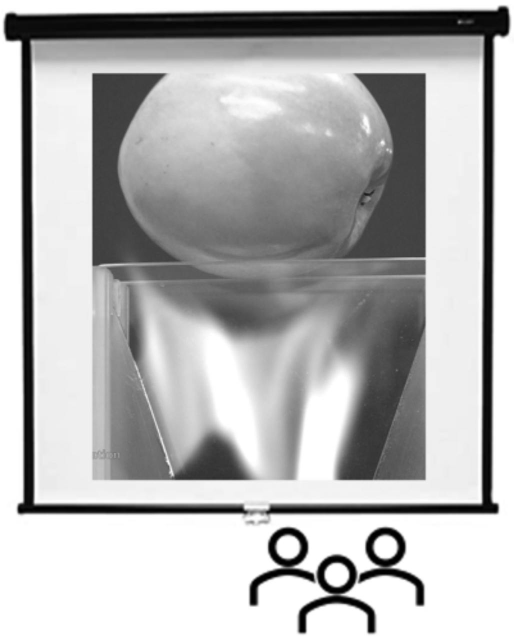


Figure 1.11 Plasma treatment of fresh produce.

Thus summarizing, the plasma technology has a lot of the success stories to present today and hopefully way more tomorrow. Most of these technologies effectively use the two key advantages of plasma, explained in the previous Section 1.4: high plasma selectivity and controllability. Obviously, not everything is so smooth with plasma technologies, surely, they have challenges sometimes very serious. The most general challenges and pathways to meet them are going to be shortly discussed below.

1.6 Electric Energy Consumption as a Challenge of Plasma Technologies, Plasma is the Future Because the Future is Electric

The success stories of plasma technology described above are mostly related to the major advantages of plasma processes, namely high selectivity, and high controllability. There is another great advantage of the plasma technologies, very high specific productivity (productivity per unit volume of reactor). As an example, for the CO_2 dissociation in nonequilibrium plasma under supersonic flow conditions, it is possible to selectively introduce up to 90% of the total discharge power into CO production when the vibrational temperature is about 4000 K and the translational temperature is only about 100 K. The specific productivity of such a supersonic reactor achieves 1 000 000 l h^{-1}, with power levels up to 1 MW. To compare, this specific productivity exceeds that of the relevant electrolytic and thermos-catalytic about 1000 times. This plasma process has been examined for the fuel production on Mars, where the atmosphere mostly consists of CO_2. On Earth, it was applied as a plasma stage in a two-step process for hydrogen production from water, as well as simply for elimination and sequestration of CO_2 from exhaust gases.

This very important feature of the **extremely high specific productivity (equipment compactness) of plasma technologies**, *three orders of magnitude above that of the conventional chemical approaches, attracts significant interest to large-scale plasma applications in chemical and environmental technologies, metallurgy, energy systems, fuel reforming and hydrogen production processes. In addition to plasma dissociation of CO_2, it includes, for example, fixation of nitrogen (NO) from air, liquefaction, and direct production of valuable organics from natural gas, plasma metallurgy, plasma stimulated waste treatment, plasma cleaning and disinfection of water, plasma activation for agriculture (stimulation of plant growth), for fresh produce washing, food processing, etc*. All these technologies are very much interested in application of plasma because of significant intensification of the processes, making equipment way more compact, as well as possibility of significant simplification of their maintenance. The wide commercialization of these plasma technologies is limited, however, today by a **major key challenge of the large-scale plasma processes, their energy cost**. While in plasma microelectronics to fabricate integrated circuits, or in plasma medicine to treat ulcers or cancers, energy cost of technology is not a crucial issue, in the large-scale chemical, environmental, and energy systems it is a crucial issue. As an example, the large-scale plasma nitrogen fixation for production of fertilizers has been successful in early 1900 but gave up to thermo-catalytic Haber–Bosch process exclusively due to energy cost competition.

Other general challenges of the plasma-based large-scale chemical, environmental, and energy systems are **scaling up, and by-products of the processes**. The scaling up challenge can be addressed by choosing discharges the most relevant for the scaling up, for example, the nonequilibrium "warm" discharges (microwave, spark, gliding arc discharges, etc.) as well as electron beams in some cases. The challenge of by-products can be addressed by choosing optimal regimes of the discharges, as well as by combination of the plasma technologies with conventional ones (like scrubbing, absorption, product separation technics, etc.). Thus, the challenges of scaling up and of by-products can be solved by the advancement in engineering, while the challenge of the electric energy cost stays as the most critical requirement for the plasma-based large-scale chemical, environmental, and energy system technologies. The large-scale plasma technologies are often still considered now as energy expensive.

Two important problems should be solved to meet the electric energy challenge of the large-scale plasma technologies. First, is absolute **minimization of the electric energy cost of the plasma processes**. Significant progress here has been achieved here recently in the large-scale plasma cleaning of exhaust gases and in the plasma metallurgy due to engineering optimization of these technologies. Second, is **decrease the cost of electricity and development of safe more environmentally friendly sources of electric energy**. It requires further development of safe nuclear and thermonuclear reactors as well as progress in large-scale development of the renewable energy sources, like solar energy, wind energy, geothermal energy, hydropower, ocean energy, bioenergy, etc. This pathway is not fast and easy to accomplish, but the end point of the path is clear. **The future is electric**, there is no alternative to that for our civilization. We move already in this direction optimizing the worldwide energy distribution. Even automotive industry is getting converted now to electric and hybrid cars and trucks. Thus, future is going to be electric, and if so, plasma and electrochemical technologies would take initiative to convert the electricity into all other human needs (now this crucial niche is kept by crude oil and oil accompanied gases). *Keeping in mind that electrochemistry today is three orders of magnitude less energy intensive and compact than plasma, we have good chances to sustain this leadership. Thus, plasma is the future because the future is electric. Good prognosis and hopes for the future, but what about today?*

1.7 Plasma Today is a High-Tech Magic Wand of Modern Technology

In many of today's practical applications, plasma technology competes with other engineering approaches and sometimes successfully finds its specific niche in the modern industrial environment. Such situation takes place, for example, in thermal plasma spraying and deposition of protective coatings, in plasma stabilization of flames, in plasma conversion of fuels, in plasma light sources, lasers, in plasma cleaning of exhaust gases, in plasma sterilization of water, in plasma activation of wash water, in plasma hydroponics, and so on. All these plasma technologies are practically interesting, commercially viable, and generally make an important contribution to the successful development of our society.

The most exciting applications of plasma, however, are related not to the aforementioned competing technologies but to those technologies which have no analogies and no (or almost no) competitors in modern industrial environment. A good relevant example is plasma applications in micro-electronics, especially for the case of etching deep trenches (at maximum 0.2 μm wide and at minimum 4 μm deep) in single crystal silicon, which is so much important in the fabrication of integrated circuits. Capabilities of plasma processing in micro-electronics are extraordinary and unique. We probably would not have computers and cell phones as we have now without plasma processing. When all alternatives fail, plasma can still be utilized; plasma chemistry in this case plays the role of **the high-tech magic wand of modern technology.**

Among other **examples, when plasma abilities are extraordinary and unique**, we can point out (i) plasma production of ozone where no other technologies can challenge plasma for more than 100 years; (ii) thermonuclear plasma reactors as a major future source of energy; (iii) low-temperature fossil fuel conversion where hydrogen is produced without CO_2 exhaust (see Section 22.10); (iv) direct liquefaction of natural gas by its incorporation into low quality usually nonsaturated hydrocarbon liquid fuels (see Section 22.12); (v) nonoxidative disinfection of fresh

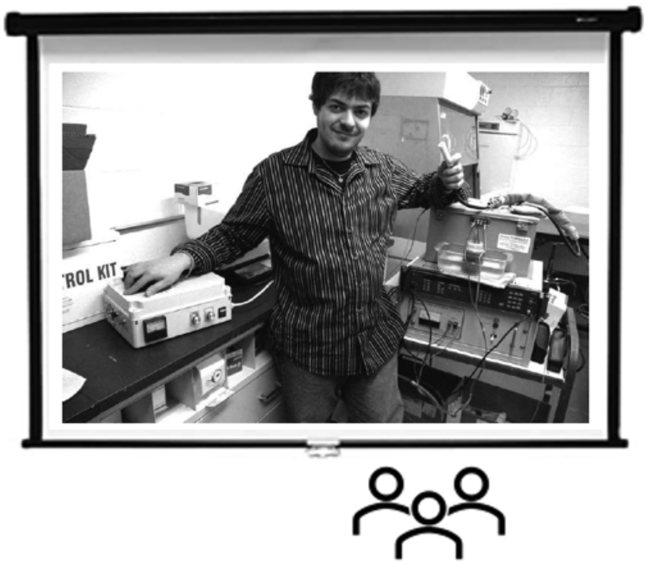


Figure 1.12 FE-DBD plasma device for direct treatment of wounds, skin sterilization, and treatment of skin diseases.

produce by plasma-activated water (see Lecture 29); (vi) synthesis of polymetric nitrogen in the cryogenic plasma of liquid nitrogen (see Section 16.7); and finally sure (vii) plasma medicine with its healing of cancers, complicated ulcers, and other diseases not effectively treated before.

In Figure 1.12, Dr. Gregory Fridman, at that time still a student of the Nyheim Plasma Institute of Drexel University, holds in his hands the pencil-like active 35-kV FE-DBD electrode, which was safely and directly applied to the human body (see Lectures 30–32), and opened possibilities to cure diseases that were previously incurable. This plasma medical device, which is in use till now in dermatological practice, even looks like a magic wand. Each type of magic, however, requires a well-prepared magician. With these words, we now can make a step from the first introductive lecture to the following ones focused on the entire scope of plasma science and technology, including most of aspects of plasma physics, plasma chemistry, plasma biomedicine, and plasma engineering.