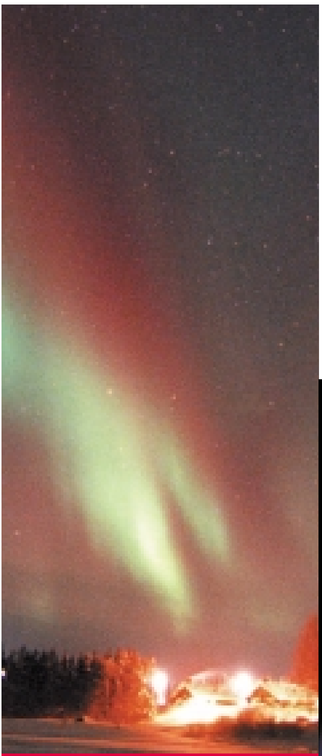
Federal Ministry
of Education
and Research

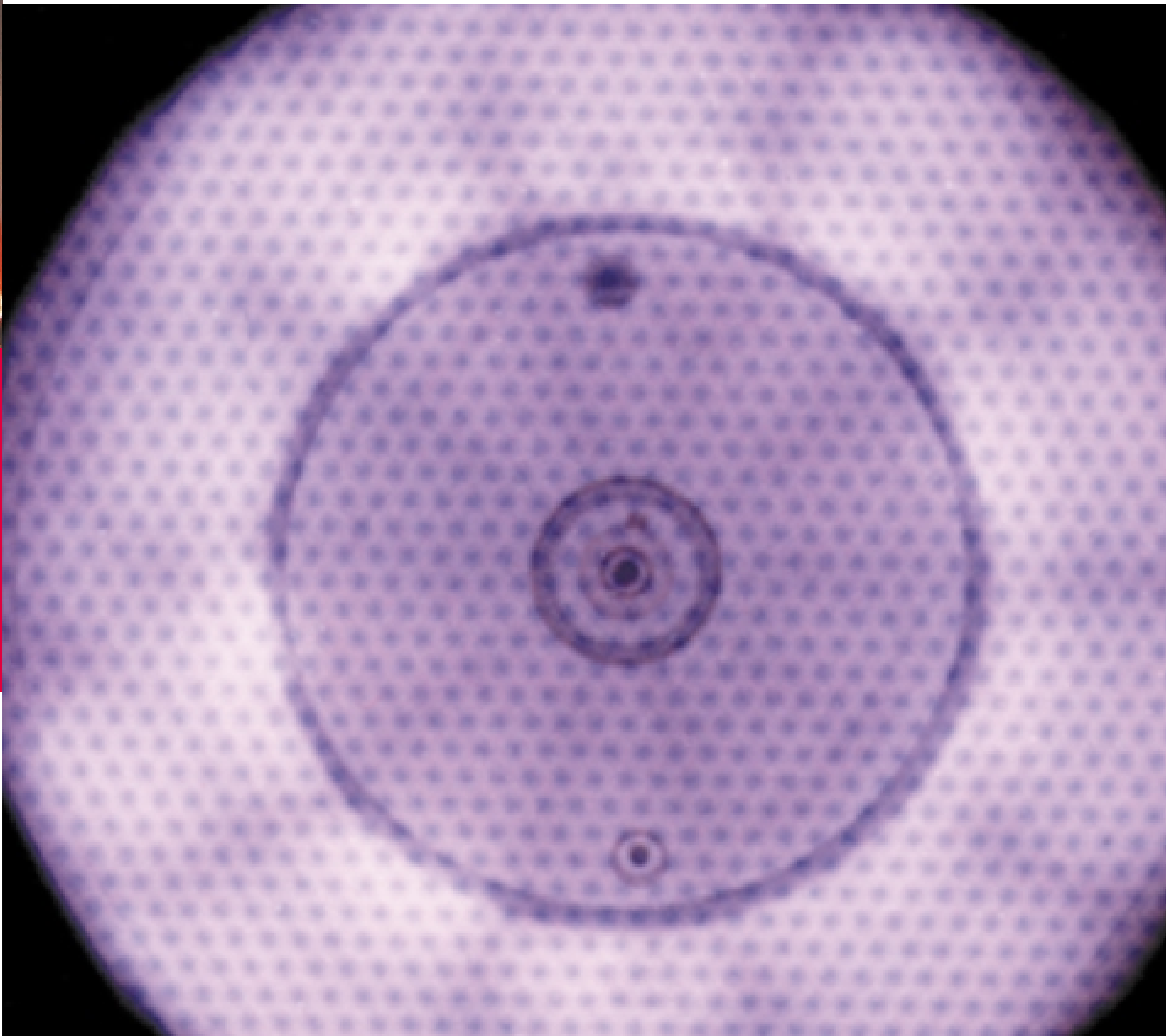
bmb+f



Plasma Technology

Process Diversity + Sustainability

BMBF PUBLIC



BMBF PUBLIC

Published by

German Federal Ministry
of Education and Research
(Bundesministerium für Bildung und Forschung –
BMBF)

Department of Public Relations

53170 Bonn
Germany

Orders
by mail to the publisher
Postbox 30 02 35
53182 Bonn, Germany
or by calling
+49-1805-BMBF02 or +49-1805-262302
Fax +49-1805-BMBF03 or +49-1805-262303
E-mail: books@bmbf.bund.de
Internet: http://www.bmbf.de

November 2001

Expert advice:
Dr. Karin Reichel
Dr. Ralf Fellenberg
VDI-Technology Center
Duesseldorf, Germany

Text:
Rolf Kickuth
Dr. Angela Lahee (Translation)
Gaiberg nr. Heidelberg
Germany

Graphics, layout, typesetting:
Agentur Rubikon
Gaiberg, Germany
http://www.rubikon.de

Printed by:
Printec Offset
Kassel, Germany

Sources of photographs and illustrations:
See inside back cover

Foreword

Plasma technology: innovations for the future

Sustainable growth and the mastering of structural change are closely linked to scientific and technical progress, to innovative capability to act, and to technological know-how.

Plasma technology, in conjunction with other technologies, provides a key to meeting these challenges to the benefit of mankind. Research in this field opens doors to promising, ecologically efficient and integrative solutions and will contribute to satisfying future needs in terms of resources and environmentally friendly processes and products.

Plasma technology is finding application in all those areas that place high demands on quality, productivity, environmental compatibility, precision and flexibility. This concerns, in particular, the provision sectors energy, environment, health and mobility, but also others.

It is especially important in the growth areas of electronics, the car-, machine- and tool-making industries, energy technology, the optics industry, and textile, environmental, and medical technology.

Because of its broad application potential, plasma technology is one of the key technologies with which innovative long-term solutions can be developed in almost all areas.

Today one can already see how plasma technology is improving the quality and performance of many products and processes. For example, plasma coating is used to produce high-quality tools and construction materials and for the surface-finishing of plastics and textiles; plasma cleaning and etching help to produce new generations of chips for high-performance computers, to make energy-saving and environmentally friendly plasma lamps, to synthesise new materials with specially designed utility value, and to dispose of or recycle toxic substances and waste materials.

The special future promise of plasma technology and its applications lies in its potential for innovation, value creation, sustainability and growth, its wide ranging opportunities for technological exploitation, and its positive environmental influences. At present, thanks to significant progress in our scientific understanding of plasma physics, plasma technology is developing into a cross-section technology whose full potential is far from being realised and whose importance is constantly growing.

In contrast, the public awareness of plasma technology remains at a very low level.

The present brochure is thus intended to give readers an overall grasp of what plasma technology is and can achieve. It aims to give an overview of the possibilities in various areas of application and of the potential for new products, energy saving, environmental protection, and job creation. Furthermore, it describes the role and significance of plasma technology and existing successful applications of plasmas, while also indicating promising areas for future activities.

The brochure addresses all those whose interest in plasma technology can be awakened or deepened; also those who see their personal future in the field of plasma research and technology, e.g. in relation to their career choice, their engagement in a new field of business or the founding of a new enterprise, or the direct exploitation of plasma technology.

The development of plasma technology will be described using a selection of current examples. Some new research topics will also be presented. Moreover, the reader will learn how and where plasma technology affects our daily lives in the form of products and processes, and where to expect new developments in the future.

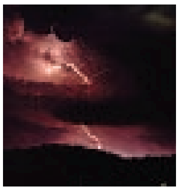
The brochure will give examples of successful projects supported by the Bundesministerium für Bildung und Forschung – BMBF (German Federal Ministry of Education and Research) but also documents the results of other research and sponsorship initiatives that have led, or are leading, to important innovations and progress in problem solving.

The choice of topics can, of course, be neither complete nor conclusive. Plasma technology is a technology of the future, a technology that can make an important contribution to sustainable growth, innovation, and new products.

The German Federal Ministry of Education and Research will continue to encourage progress in this field through the targeted support of cooperative research involving both academia and industry.

Contents

Introduction



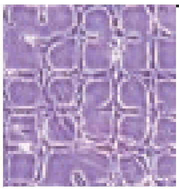
Plasma Research: From Nature to the Market

Plasmas: Omnipresent

Brighter and Further with Less Energy

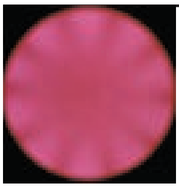
Lasting Surface Magic

Direct Benefits to Man

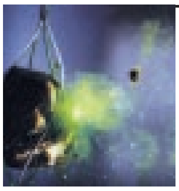


Joining and Protecting

Gentle Power

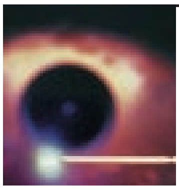


Cold Reactions



Penetrating Properties

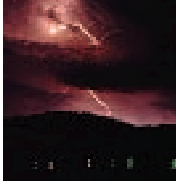
R & D Leading to New Heights



On Bonding and Boundaries

Plasma Technology in Germany

Glossary



Introduction
Plasma Research: From Nature to the Market

Northern
Lights
over Lapland

Plasma: Hot Coolness Saves Resources

Plasma is by no means a human invention. It is found in the stars - including our Sun, in the tails of comets, and in flashes of lightning. The Northern Lights, too, are a plasma phenomenon. The word 'plasma' comes from the Greek and means 'form' or 'shape', but also 'that which is formed'. Incidentally, the cell-free fluid of the blood and also a semiprecious stone, a type of jasper, also bear the name 'plasma'.

Technical plasmas today find a wide range of applications in the most diverse branches of manufacturing, including the production of many modern household objects. These manifold applications owe their existence to intensive research and development work in this young field of technology.

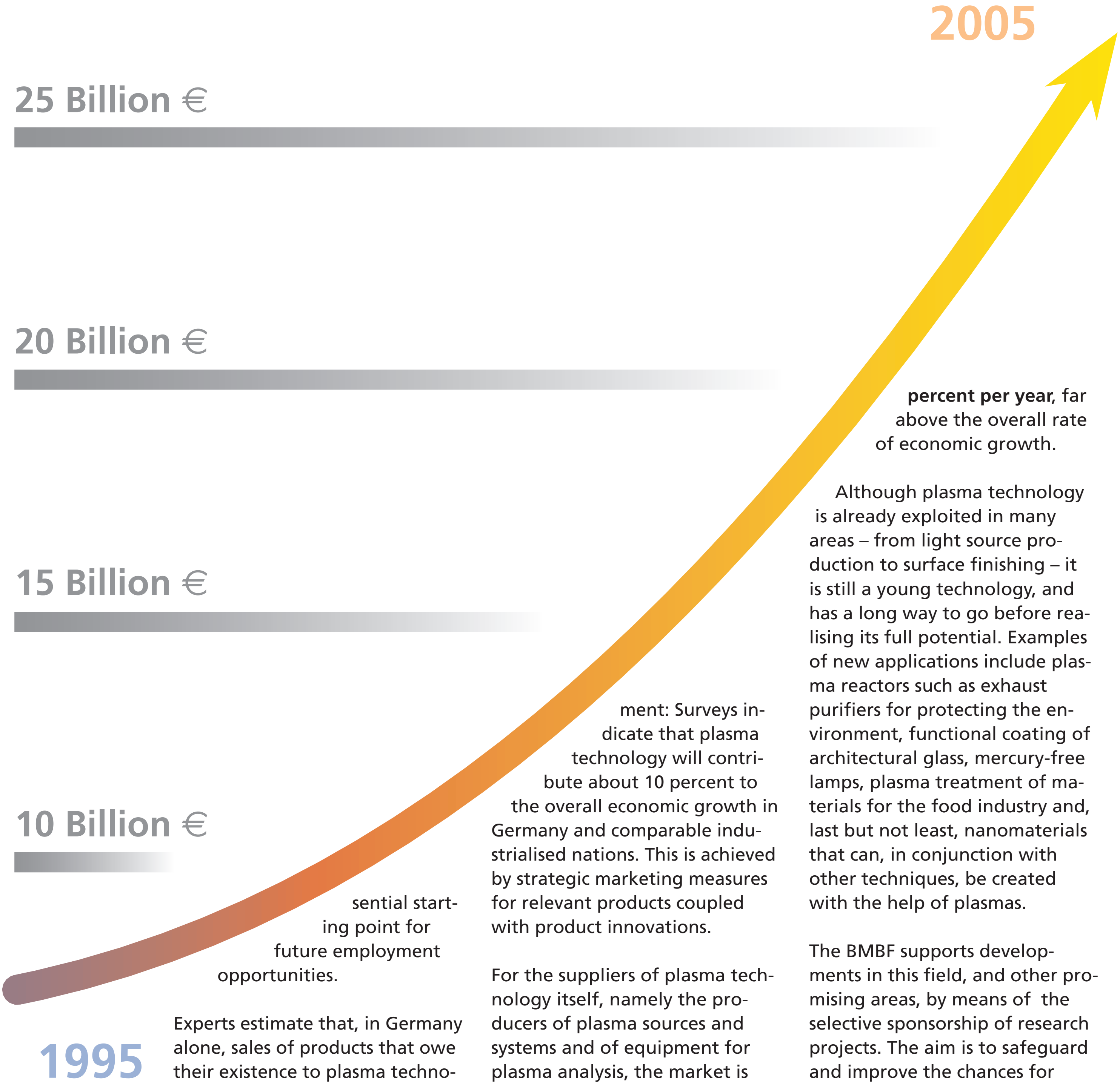
Due to the complicated and expensive processes needed to produce plasma, usually via electrical discharges in evacuated glass chambers, and also because of the complexity of the phenomena themselves, for a long time plasma physics remained a relatively exotic research endeavour. However, progress in our understanding of the physical processes involved in plasmas has now given birth to an interdisciplinary technology of unrivalled potential. One of its major benefits relates to the sustainable use of raw materials and energy, an advantage both for the environment and for the economy. Great flexibility and inherent safety are further plus points associated with plasma processes.

Plasma is often referred to as the fourth state of matter. When a solid material is heated, it typically transforms first into a liquid and, at a higher temperature, into a gas. If further energy is supplied to the gas, it becomes electrically conducting, even though overall electrical neutrality is maintained. This is due to the fact that the electrons gain sufficient energy to separate from the atoms or molecules of the gas. The plasma thus consists of a mixture of mainly positively charged ions, electrons, and neutral particles.

Now we can appreciate a most important property of non-thermal low-temperature plasmas and the one which be decisive in the applications described here (the high temperature plasmas used in fusion research will not be discussed): Whilst the temperature of the ions and neutral particles is usually less than one-hundred degrees Celsius, the energy of the electrons in such a plasma corresponds to a temperature of some 10 000 degrees Celsius! Thus they serve as highly reactive tools for powerful but gentle applications without consuming great energy. This 'hot coolness' opens the way to undreamt-of processing possibilities and enormous economic opportunities.

The enormous promise of plasma technology stems from its remarkable potential for environmentally friendly and energy-saving processing; its low processing temperatures; its flexibility and broad spectrum of applications; and its **clear ecological advantages**. These factors predestine plasma technology for sustainable development and, via innovative products and processes, open the way to **new business opportunities**. This is particularly the case for small and medium-sized innovation-oriented companies. In this way, plasma technology will represent an essential starting point for future employment opportunities.


Plasma cleaning of copper tubes

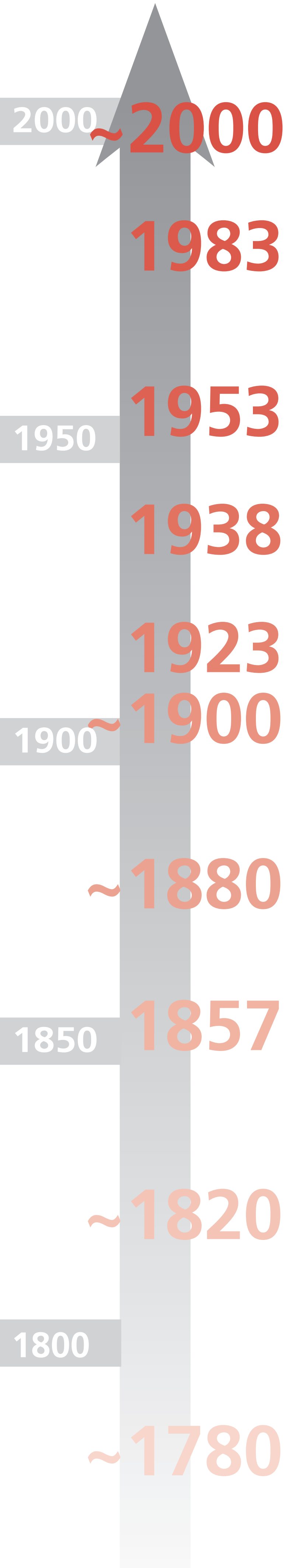


Experts estimate that, in Germany alone, sales of products that owe their existence to plasma technology now amount to about 45 billion Euro per year; worldwide the annual value is placed at about 500 billion Euro. Here one should pay particular attention to the potential of plasma technology for the overall economic development: Surveys indicate that plasma technology will contribute about 10 percent to the overall economic growth in Germany and comparable industrialised nations. This is achieved by strategic marketing measures for relevant products coupled with product innovations.

For the suppliers of plasma technology itself, namely the producers of plasma sources and systems and of equipment for plasma analysis, the market is of course somewhat smaller. In 1995 worldwide sales of such products were approximately seven billion Euro; in 2005 they are expected to reach 27 billion Euro. This represents **an average growth rate of 15 percent per year**, far above the overall rate of economic growth.

Although plasma technology is already exploited in many areas – from light source production to surface finishing – it is still a young technology, and has a long way to go before realising its full potential. Examples of new applications include plasma reactors such as exhaust purifiers for protecting the environment, functional coating of architectural glass, mercury-free lamps, plasma treatment of materials for the food industry and, last but not least, nanomaterials that can, in conjunction with other techniques, be created with the help of plasmas.

The BMBF supports developments in this field, and other promising areas, by means of the selective sponsorship of research projects. The aim is to safeguard and improve the chances for innovative German high-tech companies active in this area. Frequently these are small or medium-sized companies, many of them developing in the environment of an university or national research laboratory.



~2000 **In Germany alone, well over 200 companies are active in the field of low-temperature plasma technology.**

1983 **In Japan, substrates are coated with polycrystalline diamond layers in a microwave plasma.**

1953 **Werner Schmellenmeier discovers diamonds as a product of acetylene gas discharges.**

1938 **Fluorescent lamps become commercially available.**

1923 **Irving Langmuir discovers plasma oscillations**

~1900 **Joseph John Thomson reveals the nature of cathode rays. Eugen Goldstein demonstrates the existence of 'canal rays'.**

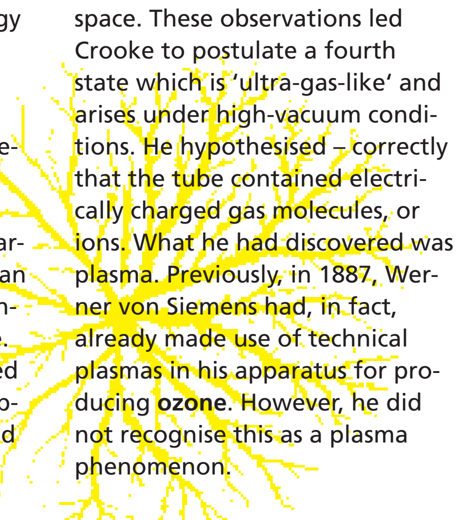
~1880 **William Crookes discovers plasma.**

1857 **Werner von Siemens develops the ozoniser, the first application of technical plasmas.**

~1820 **Michael Faraday discusses the possibility of a fourth state of matter.**

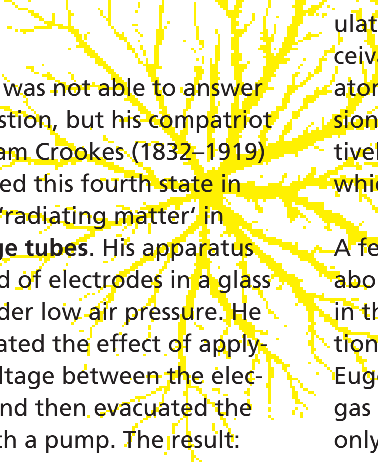
~1780 **Georg Christoph Lichtenberg first generates the patterns that bear his name (background pictures on this page).**

A Glance Back at the Dark Spaces



The history of plasma technology goes back to the 18th century. It was the physicist and writer Georg Christoph Lichtenberg (1752–1799), professor of mathematics in Göttingen from 1770, who first generated and documented beautiful surface discharges. This he did by introducing an insulating sheet between a pointed electrode and a metal plate. When fern spores were scattered onto this sheet and a voltage applied between the electrode and the metal, brush discharge patterns were formed.

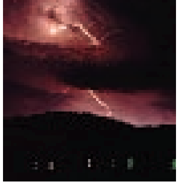
Lichtenberg's experiments merely displayed a phenomenon; the first attempts to explain it in terms of the plasma state were due to the experimental physicist from London, Michael Faraday (1791–1867). Prior to his groundbreaking discovery of electromagnetism in 1821, he spent the years 1816–1819 investigating the properties of heated matter: What happens when a material is heated from the solid via the liquid to the gas phase and beyond? Is there a **fourth state of matter?**



Faraday was not able to answer this question, but his compatriot Sir William Crookes (1832–1919) discovered this fourth state in 1879 as 'radiating matter' in **discharge tubes**. His apparatus consisted of electrodes in a glass tube under low air pressure. He investigated the effect of applying a voltage between the electrodes and then evacuated the tube with a pump. The result: the remaining gas began to glow green and developed a pattern of stripes. Furthermore, at the negative electrode, the cathode, he observed a dark region, still known today as Crookes' dark space. These observations led Crooke to postulate a fourth state which is 'ultra-gas-like' and arises under high-vacuum conditions. He hypothesised – correctly that the tube contained electrically charged gas molecules, or ions. What he had discovered was plasma. Previously, in 1887, Werner von Siemens had, in fact, already made use of technical plasmas in his apparatus for producing **ozone**. However, he did not recognise this as a plasma phenomenon.

A better understanding of the processes occurring in gas discharge tubes was obtained through the experiments of Sir Joseph John Thomson (1856–1940) in Cambridge. In 1897 he published a paper reporting that cathode rays undoubtedly consist of tiny negatively charged particles, which he called corpuscles. He determined the charge-to-mass ratio of these particles, which were later to become known as electrons. On account of their tiny size in comparison with atoms, he postulated that they could quite conceivably by a constituent of the atom. This led him to the conclusion that atoms consist of positively charged mass 'throughout which electrons are distributed'.

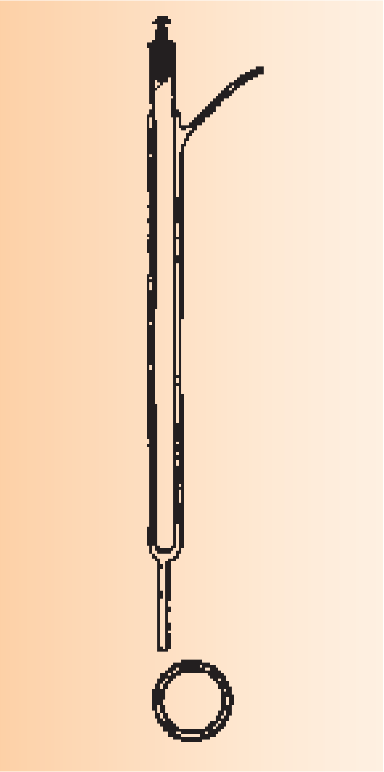
A few years later Thomson's ideas about the electron and its role in the atom received confirmation: In 1886, the German chemist Eugen Goldstein proved that a gas discharge tube contains not only cathode rays (electrons) but also other rays that travel in the opposite direction towards



the anode. He called these canal rays. Shortly thereafter they were shown to be positively charged atomic particles, the ions; in other words, particles with missing electrons. Thus plasma had been identified as a mixture of electrons and ions.

Now only the name was missing. This was provided by the New York chemist Irving Langmuir (1881–1957). In 1923 Langmuir observed, in an ionised gas, characteristic oscillations that depended on the electron density and mass. These collective oscillations in a system of many charged particles he called **'plasma oscillations.'** They arise from random inhomogeneities in the charge distribution in plasmas – local regions of higher electron or ion density – and the natural tendency of the charge to redistribute uniformly.

The first attempt to give a full account of gas discharges was published by the German physicist Johannes Stark in 1902 with the title 'Electricity in Gases'. As director of the physics institute of the University of Greifswald, he was awarded the Nobel Prize on 10th December 1919 for his discovery of the Doppler effect in canal rays and the splitting of the spectral lines in electric fields. At the end of 1918, Stark invited Rudolf Seeliger to Greifswald. Seeliger worked there until 1955, winning recognition as one of the pioneers of modern plasma and gas-discharge physics.



The ozoniser consisted of two glass tubes, one inside the other. In the air-filled space between the tubes it was possible, using an induction apparatus with a Wagner interrupter and metal layers on the tube walls, to generate a plasma that ozonised the air. (Sketch taken from the 1889 book 'Scientific and Technical Works of Werner Siemens' [in German], published by Julius Springer, Berlin).

More recently great interest has been aroused by the generation of diamond layers. In 1953, at the teaching university in Potsdam, Werner Schmellenmeier identified **diamonds** as a product of acetylene gas discharges. In the 1960s and 1970s techniques were developed in Russia for chemically precipitating diamond layers from the gas phase and, in 1983, Japanese scientists succeeded in producing diamond layers with a microwave plasma.

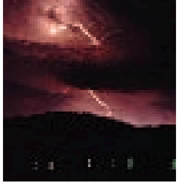
Variety is the Spice ...

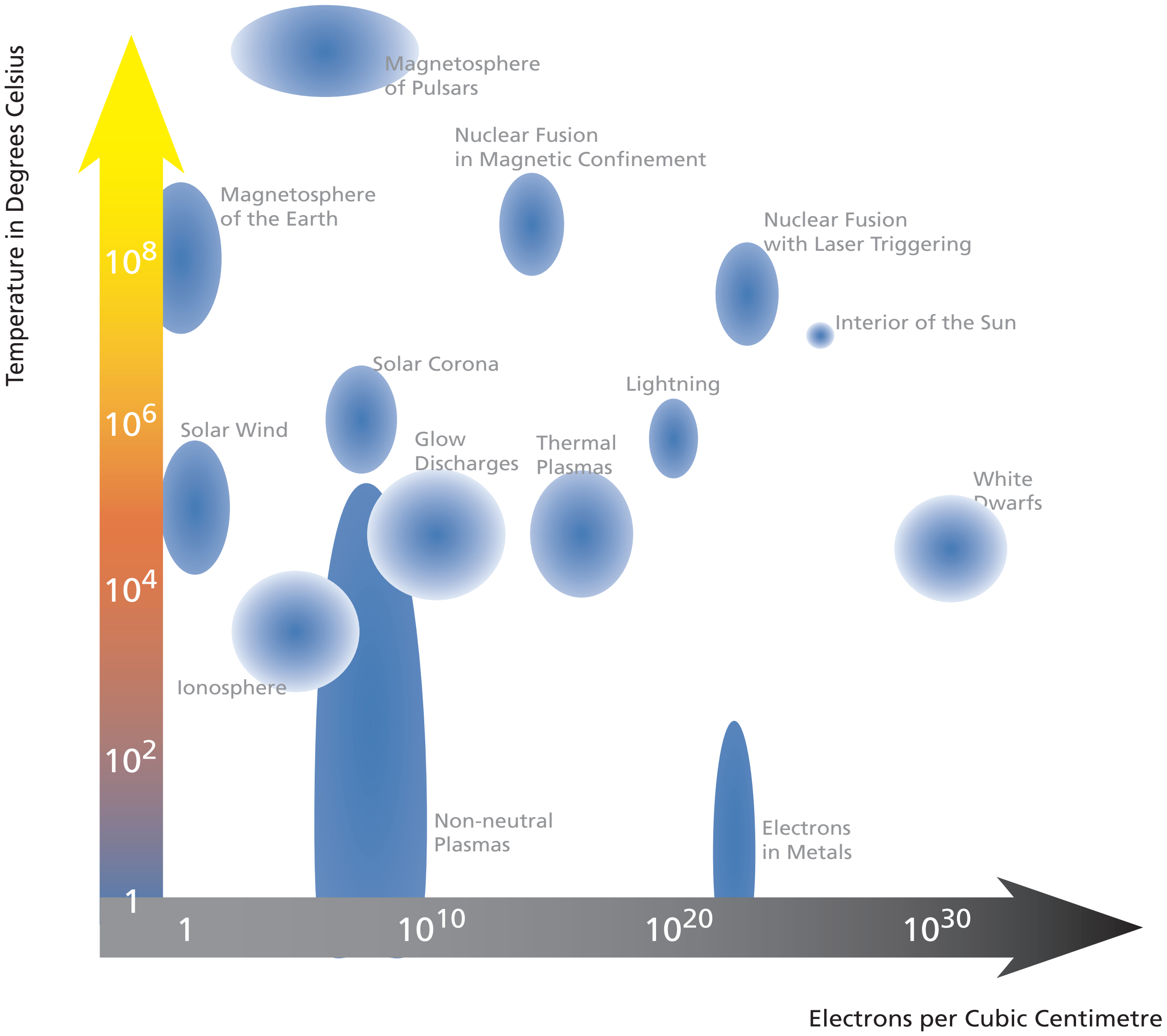
Plasmas are fundamentally different depending on whether or not they are in thermal equilibrium. The question is: do all the particles have the same temperature, the same energy, or – expressed pictorially – do the lightweight particles dash around in a soup of more inertial heavyweights? In the former case, one speaks of an **equilibrium** or **thermal plasma**; typical equilibrium plasmas are those present inside stars. In the latter case, we are dealing with **non-thermal plasmas**. In general the **low-temperature plasmas** are of this type and it is their remarkable applications and further promise that will be described in this brochure.

Plasmas are generated in gases by heating, by applying a voltage, or by injecting electromagnetic waves. The results is that the gas particles, the atoms and molecules, begin to move faster in the three spatial dimensions but simultaneously acquire higher rotational and vibrational energies. Due to collisions between the particles, the atoms and molecules are 'pulled apart', giving rise to the (mainly) positively charged ions on the one hand, and to electrons that are freed from the atoms and molecules on the other.

Depending on the method of generation used, the plasma can display a broad spectrum of states ranging from extreme nonequilibrium to almost complete thermal equilibrium.

Plasma parameters – both those of natural plasmas and those of





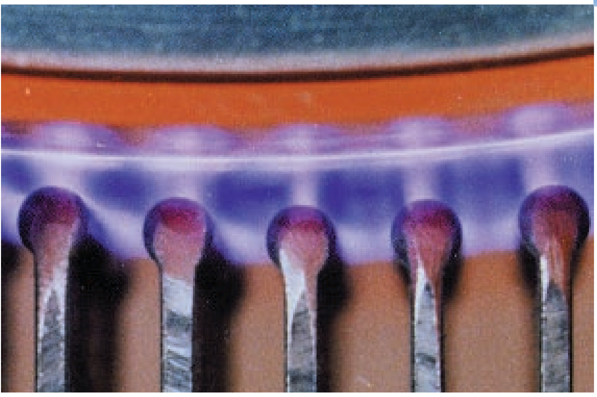
Diverse types of plasma, represented in terms of the parameters electron density and temperature

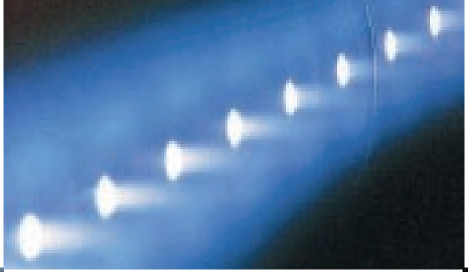
technical plasmas – span a wide range of values. The electron density, for example, can vary between one and 10^{25} electrons per cubic centimetre, thus reaching values higher than those found in metals. The mean free path of the particles, i.e. the average distance they travel before colliding with another particle, can be tens of million kilometres but also merely a few micrometres.

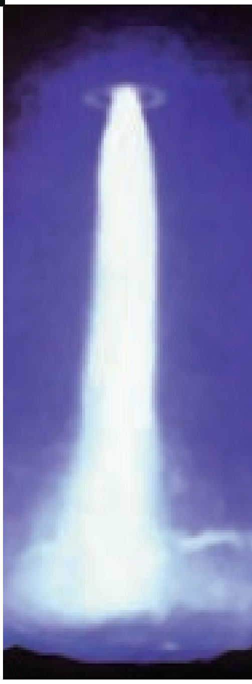
Of particular interest for technological applications are the nonequilibrium plasmas because, in these, it is possible to separately control the temperature of, on the one hand, the ions and neutral particles, and, on the other, that of the electrons. It is mainly the energy of the electrons, however, that is important for initiating chemical reactions. If one varies the conditions under which the plasma is generated by choosing different starting gases, energy input or reactor geometries, one creates the possibility of a wide range of applications in technical processes. Herein lies the great benefit of low-temperature plasma technology, which relies, in general, on low-energy nonequilibrium plasmas.

For a long time, the low-temperature plasma physics describing such plasmas remained very much in the shadows. Its significance for fundamental research and technical exploitation was not adequately recognised. In part this was due to the fact that these plasmas are extremely complex many-particle systems with a huge number of component particles and states. Furthermore, they are governed by complicated nonlinear dynamics, involve collective interactions, and are strongly inhomogeneous and rapidly changing systems, also displaying plasma–material interactions.

Nonthermal plasmas are thus anything but easy to calculate and present a real challenge for science and engineering. In the meantime, however, numerous approaches have been developed for controlling and regulating







Photos above (from left to right): glow discharge; barrier discharge at atmospheric pressure; HF plasma source; direct-current arc on steel

the internal parameters of such plasmas.

Sources for Wide-Ranging Applications

Plasma sources differ greatly from one another; some operate at very low gas pressures, others at atmospheric pressure. The plasmas can be excited by direct or alternating current, or by the effect of high-frequency electromagnetic fields. Plasma sources can be operated either continuously or in pulsed mode. If one applies a voltage between two electrodes extending into a nearly evacuated glass tube, under appropriate conditions a plasma will ignite; in this case, it is known as a glow discharge. The ignition is brought about by the small fraction of charged particles always present in the gas. Accelerated by the applied voltage, their subsequent collision processes cause an avalanche-like increase in the number of charge carriers.

If the discharge current generated by this avalanche effect in a glow discharge is increased by applying ever higher voltages to the electrodes, the negative electrode, the cathode, undergoes strong heating due to its bombardment with positive ions. The electrons in the metal of the cathode thereby gain sufficient energy to escape from the solid.

The discharge then changes abruptly into an arc discharge. Here one encounters much higher currents than in a glow discharge; the cathode heats up to a few thousand degrees Celsius and also influences the composition of the plasma. The plasma itself is now referred to as an arc plasma. Modern applications of such plasmas include the powerful headlights of top-of-the-range limousines, but industry, too, exploits arc plasmas: scrap steel, steel alloys and high-melting-point metals such as titanium, tantalum, molybdenum and niobium are melted with plasma burners operating in the megawatt range.

At atmospheric pressure – an important condition, for example, for continuous processes – one can also generate corona or barrier discharges. Corona sources contain inhomogeneous initial electric fields, formed, for example, around pointed electrode elements. Barrier discharge sources are characterised by the presence of insulating layers on one or both electrodes, or in the gas-filled gap between the electrodes. Both these sources allow the production of large-area plasmas, corona discharges having a strong filamentary character, whereas barrier discharges are significantly more homogeneous.

The application of high-frequency fields is a further method of generating plasmas in suitable vessels (HF sources). As in the case of direct-current plasma sources, the ignition of the plasma depends on the naturally occurring charge carriers being able to acquire energy so as to ionise further atoms. This energy is transferred by the interaction of the high-frequency field with the electrons, which, since they are very light, can follow the rapidly changing field. The plasma–wall losses can be reduced by applying an external magnetic field to the high-frequency plasma.

Microwave plasmas – like microwave ovens – transfer energy using electromagnetic oscillations at a frequency far above the above-mentioned high frequency, but below the frequency of thermal radiation. This type of plasma source can be used to create high plasma densities and, because of its low ion energies, is particularly well suited for non-destructive surface processing.

Microwave plasmas, too, can be readily controlled with the help of magnetic fields. The relevant equipment is known as an ECR plasma source (electron cyclotron resonance heating). Here, the energy is channelled specifically into the electrons in the plasma. ECR discharges are particularly clean and homogeneous, a feature that is invaluable in the manufacture

Plasmas: Omnipresent

The rapid growth of plasma technology is reflected in applications that are today already making our daily lives more convenient and healthier. The unobtrusive way in which our lives and environment are being enriched with products that benefit from plasma processes or, indeed, owe their very existence to such processes, goes hand in hand with a characteristic trait of plasma technology: Sustainable use of raw materials and energy, leading to products that are durable and of lasting value.

Today one already constantly encounters plasma-treated products, for example products that have been cut by plasma burners or have been coated in a plasma. As sources of light in the darkness, plasma phenomena in high-tech lamps are demonstrating that light production can increasingly be decoupled from heat production. More and more products are appearing whose astonishing properties are born in plasma processes that selectively influence the molecular structure of the component material, for example the degree of cross-linking of polymers.

Even T-shirts, jumpers and woollen socks will soon bear witness to the improvements possible with plasma technology: Plasma treatment is able to produce felt-free wool without, as was the case until now, resorting to the use of chemicals that contaminate the environment.

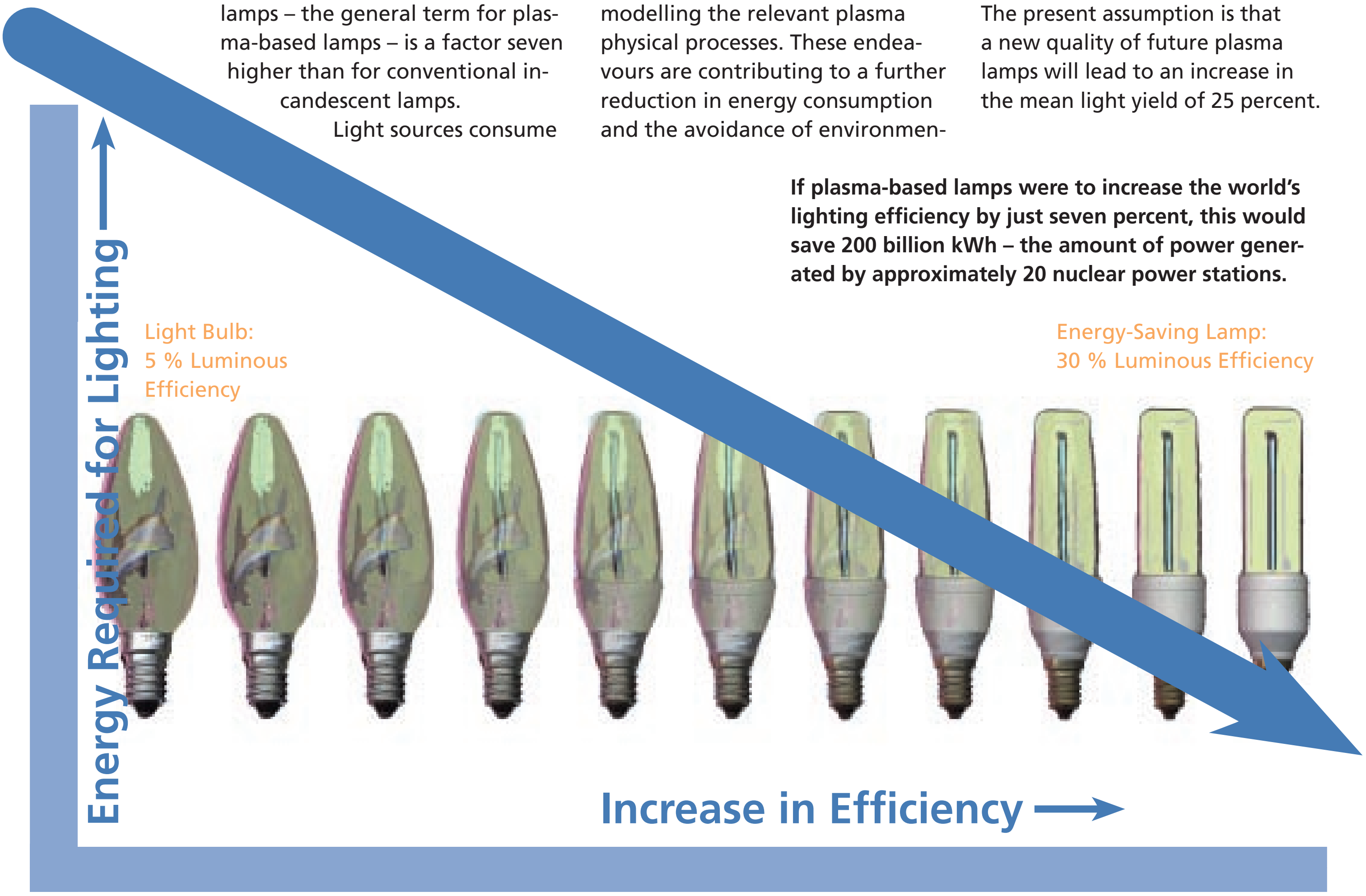
Brighter and Further with Less Energy

Saving without Sacrifice

Modern lamps are both literally and metaphorically a shining example for the influence of plasma technology in our immediate surroundings. But at the same time they are evidence of its ‘invisibility’: With the usual expression ‘fluorescent tube’, one stresses the process of light conversion rather than that of light generation, as would be implied by the name ‘plasma tube’. Nonetheless, these products of our daily lives are reliant on plasmas and are becoming increasingly effective in their benefits for man, while simultaneously helping to protect the environment. For example, the **luminous efficiency** of gas-discharge lamps – the general term for plasma-based lamps – is a factor seven higher than for conventional incandescent lamps. Light sources consume eight percent of Germany’s electrical energy. Therefore 45 percent of the total energy is consumed for lighting purposes by discharge lamps, which already provide 80 percent of the total light required in this country. The larger remaining part of the energy is taken up by thermal radiators such as incandescent lamps, which dissipate more as heat than as light. However, even discharge lamps only attain one third of the theoretical luminous efficiency at present. Furthermore many of today’s lamps contain mercury – albeit in minute quantities. Thus there is still significant room for improvement here; the BMBF is therefore supporting fundamental physics research aimed at explaining and modelling the relevant plasma physical processes. These endeavours are contributing to a further reduction in energy consumption and the avoidance of environmentally harmful substances, such as mercury. To illustrate the environmental impact of lamp technology, one need only consider the following figures: World-wide more than ten billion lamps are produced each year; these have a corresponding value of about 12 billion Euro. Around 1990, the global consumption of electrical energy for lighting purposes was 3000 billion kilowatt hours.

Based on these figures, an increase in the average luminous efficiency of just seven percent would mean a reduction in **carbon dioxide (CO_2) emission** of about 500 million tonnes per year. This is approximately twice the annual CO_2 emission of all German power stations! The present assumption is that a new quality of future plasma lamps will lead to an increase in the mean light yield of 25 percent.

If plasma-based lamps were to increase the world’s lighting efficiency by just seven percent, this would save 200 billion kWh – the amount of power generated by approximately 20 nuclear power stations.



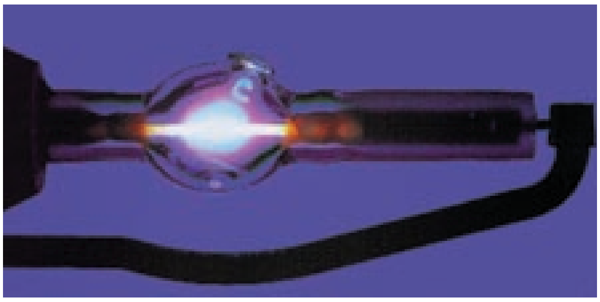
Brighter and Further with Less Energy

High Luminous Efficiency, Bright, True Colours

Pleasing to the human eye is natural light. In analogy to this, artificial light should have sufficient brightness and be able to reproduce true colours. Theoretically, the maximum possible efficiency of a white light source is 280 lumens per watt – theoretically …

To get as close as possible to this value, lamp developers are continually testing their ingenuity. Around 70 years ago, they already hit upon the idea of applying alternating electric fields to generate gas discharges in glass tubes with relatively low energy consumption. Mercury vapour turned out to be a readily excitable medium. In order to optimise other electrical characteristics, a further buffer gas, usually argon, was added to the low-pressure tubes. Unfortunately, the excited mercury vapour emitted predominantly ultraviolet light. To overcome this problem, the inside of the tubes was coated with a fluorescent substance that converts ultraviolet into visible light; hence the name ‘fluorescent tube’, a type of lamp that has been commercially available since 1938.

None the less, such **low-pressure plasma lamps** still possess significant potential for improvement. Probably the greatest success in this field since the 1980s is the now widely used energy-saving lamp. In essence this is simply a folded fluorescent tube. It contains a voltage and frequency converter which delivers an alternating voltage at some tens of kilohertz, a better range suited for plasma generation.



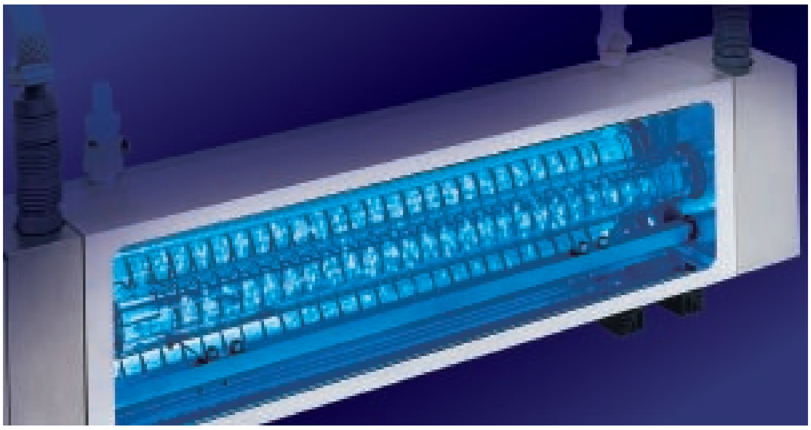
Above: The high-pressure gas-discharge lamp typically outlives the vehicle that it serves and produces a bright light similar in quality to daylight.

The latest development in low-pressure plasma lamps even manages to avoid the use of mercury; it works instead with excimers. This mysterious sounding name originates from the term ‘excited dimer’ and refers to electronically excited molecule complexes. These are extremely short-lived entities which, when they decay, emit high intensity and nearly monochromatic ultraviolet radiation. Numerous different kinds of excimers are known enabling one, through the choice of a suitable gas mixture, to generate radiation in many wavelength regions. However, in developing lamps that exploit this principle, there still remains the difficulty of finding a suitable phosphor to convert a maximum amount of UV radiation into white light.

One of the first applications of such a light source is in the backlighting for computer LC-displays. The mercury-free lamp is twice as bright as conventional display lamps and has a lifespan of up to 100 000 hours, or more than 11 years.

Going beyond the light source, the excimer lamp can also be used, for example, in selective photochemical processes, and in the fine cleaning of surfaces or of prepurified water. The very short wavelength of the ultraviolet radiation of such lamps – typical wavelengths are 308, 222 or even 172 nanometres – is so high in energy that it can split molecules of pollutants such as chlorinated hydrocarbons or even cyanide in effluent and convert these into harmless molecules such as water and carbon dioxide. This opens up alternatives to the use of hydrogen peroxide or ozone for water purification, but only in certain special cases. Because this extremely short wavelength radiation penetrates only a short distance into water, it will probably only be possible to build reactors that process a few cubic metres of water each day.

When used for surface processing, for example in the hardening of printed inks, excimer beams do not cause the irradiated surface to heat up. This has the advantage that even tem-



Left: Excimer lamp for technological processing applications

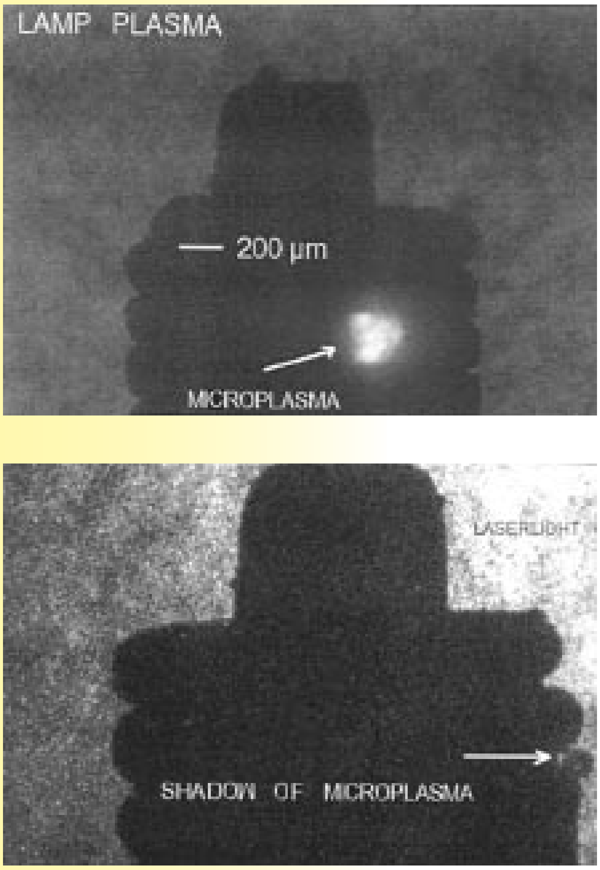
perature-sensitive materials can be illuminated with intense UV excimer radiation.

The historical roots of **high-pressure plasma lamps** go back even further than those of their low-pressure relatives, namely to the electric arc. The latter was discovered in 1812 by the Englishman Humphrey Davy and used in the same century for illumination purposes in the form of carbon arc lamps. Today, the latest mass-produced high-pressure plasma lamps are a much discussed topic among car drivers: Their bright illumination, similar in quality to daylight, is initially perceived by many as a dazzling bluish light especially at night. These lamps operate at a pressure some ten times that of the atmosphere. Their luminous density can exceed that of the Sun! Lamps of this kind have been in use for years to illuminate large squares, sports stadia, and streets. Their luminous efficiency can reach more than 120 lumens per watt.

Present research on plasma lamps is aimed, among other things, at reducing the losses that occur when excited atoms and molecules collide with the arc tube wall materials, increasing the useful lifetime of electrodes or even avoiding electrodes, and also finding better phosphors. The BMBF supports fundamental research in both low- and high-pressure plasma lamps. Important targets are the complete avoidance of mercury in these lamps and the further improvement of their efficiency.
Still among the more exotic light sources are molecular light emitters such as the sulphur lamp, in which microwave radiation produces a plasma in gaseous sulphur, giving rise to illumination of a quality similar to daylight. The complete lamp, however, is complex and until now only suited for large scale illumination. Efforts are thus underway to find other molecules that are suited for use in molecular light emitters. Another object of current research are microwaveexcited clusters of several thousand tungsten atoms, which also emit a spectrum of light similar to daylight.

Lamp Research

The meticulous work demanded of researchers involved in developing lamps is illustrated by the challenges facing plasma analysis: It is necessary to monitor processes occurring on a nanosecond time scale; a time in which light travels a mere 30 centimetres ...



In high-pressure lamps, one observes a flickering of the discharge at the cathode, during which its material is more strongly and non-uniformly removed. Sophisticated techniques have been used to reveal some unexpected phenomena: microplasmas are formed from the surface material of the hot cathode. The upper picture is a highly magnified image of such a cathode, consisting of a tungsten coil and, below, a tungsten winding containing a material that supports electron emission. The photo was taken with an exposure time of just five millionths of a second so that the luminous plasma of the lamp, and likewise the glowing cathode, are scarcely visible. Bright and clearly visible, however, is a microplasma on the coil. In the lower picture, it has migrated to the edge of the coil. This picture had an even shorter exposure time of half a billionth of a second. To enable one to see anything at all, the electrode region was illuminated from behind with a powerful laser. The electrode appears as a silhouette and the dense laser-light-absorbing microplasma also throws a shadow. These images give insight into the processes in the electrode region. The overall aims of the investigation are to achieve a longer life span and lower energy consumption, whilst maintaining the good illumination properties of the gas discharge lamps.

Brighter and Further with Less Energy

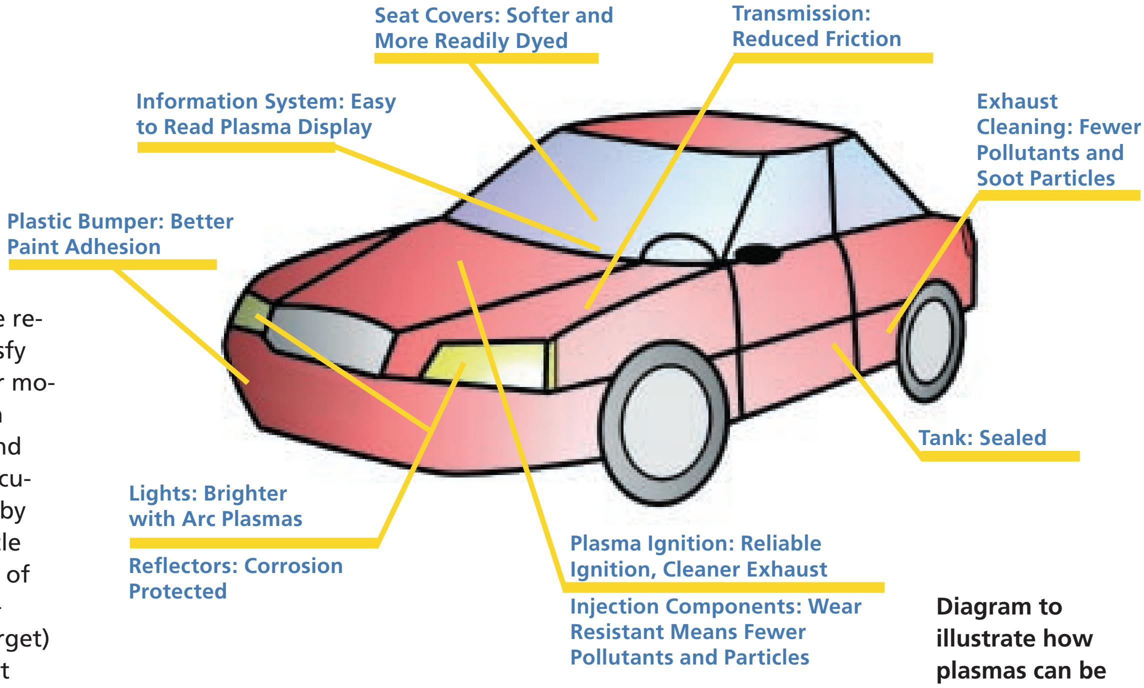


Diagram to illustrate how plasmas can be used, directly, or indirectly during the manufacture, to make cars more environmentally friendly, while at the same time improving many features

Environmentally Acceptable Mobility

Today's car manufacturers are required to simultaneously satisfy disparate demands: A greater mobility must be reconciled with lower energy consumption and lower exhaust emission. Particularly strict limits are imposed by the **Euro IV Standard**. A vehicle that requires only three litres of fuel per 100 kilometres (a demanding but now realistic target) while providing good comfort and safety is a major challenge for the automotive industry.

Plasma technology makes a significant contribution to achieving this aim. It will help to reduce the fuel consumption of the engine, to make the headlights brighter and to make the exhaust gases cleaner. Plastic fuel tanks can be sealed using microwave discharges to avoid leakage. Corona discharges make the seat covers softer and easier to dye; furthermore the use of dyes containing heavy metals can be avoided. Plastic components such as bumpers have better paint adhesion when the surfaces are pretreated with high-frequency discharges.

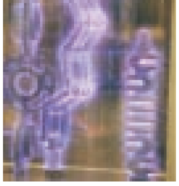
In the engine and transmission, plasma-hardened high-temperature materials yield reduced friction in operation, thus improving the efficiency. Drivers are assisted in the traffic jungle by information systems with easy-to-read plasma displays.

Of the innovations for vehicles of the future, two are particularly interesting here, since plasma plays a central role. One is to be found in the heart of the internal combustion engine, in the combustion chamber of every cylinder. In future, one may encounter here a **plasma ignition**. In fact, even conventional spark plugs generate a plasma with every spark. However, the principle of plasma ignition exploits a different ignition mechanism, one that occurs on a nanosecond time scale.

Numerous advantages are associated with such an ignition mechanism: The electrodes can be so arranged that no parts protrude into the combustion chamber. A plasma beam reliably reaches the layers of ignitable mixture in the carefully mapped combustion regions, especially in modern direct-injection petrol engines. Plasma ignition thus provides more efficient energy transfer than other forms of ignition. The reliable ignition also improves the exhaust properties of modern engines.

Another possible future development is the inclusion, in every petrol- or diesel-fuelled car, of a **plasma reactor in the exhaust system**. In engines that must operate with an excess of oxygen – diesel engines and modern lean-burn engines – it is not possible to use conventional three-way catalytic converters. These engines thus pump significant quantities of nitrogen oxides into the environment. Even the normal car with its three-way catalytic converter has its weak points in this respect: After starting the engine, the catalytic converter is still cold and works only poorly.

The problems sketched above can all be tackled with the help of plasma technology in conjunction with suitable catalytic converters. A plasma reactor that generates pulsed barrier discharges at atmospheric pressure can convert unburned hydrocarbons, carbon monoxide and nitrogen oxides into nontoxic gases. Even the soot particles in diesel exhaust can be made harmless. These processes all take full effect from the moment the engine starts. Such plasma reactors are still in the development phase however. Fundamental work in this area is supported by the BMBF. The aim is to reduce the consumption due to reactor operation and to make the exhaust gases nontoxic.



Activated for New Contacts

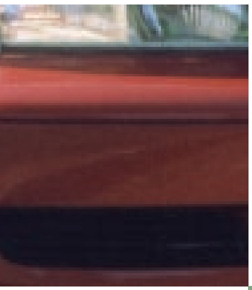
The properties of the various particles in plasmas change dramatically when these come into contact with solid material; such encounters are associated with losses of energy and charge. But the energy is not lost without trace. In fact the energy is transferred to the surface of the material in a very special plasma-specific manner. Plasmas are actually particularly well suited for surface treatment. On the one hand they can activate a surface, i.e. the molecular components of the surface are made receptive to bonding with other substances. On the other hand, by a suitable choice of process gases, plasmas can serve to coat the surface directly.

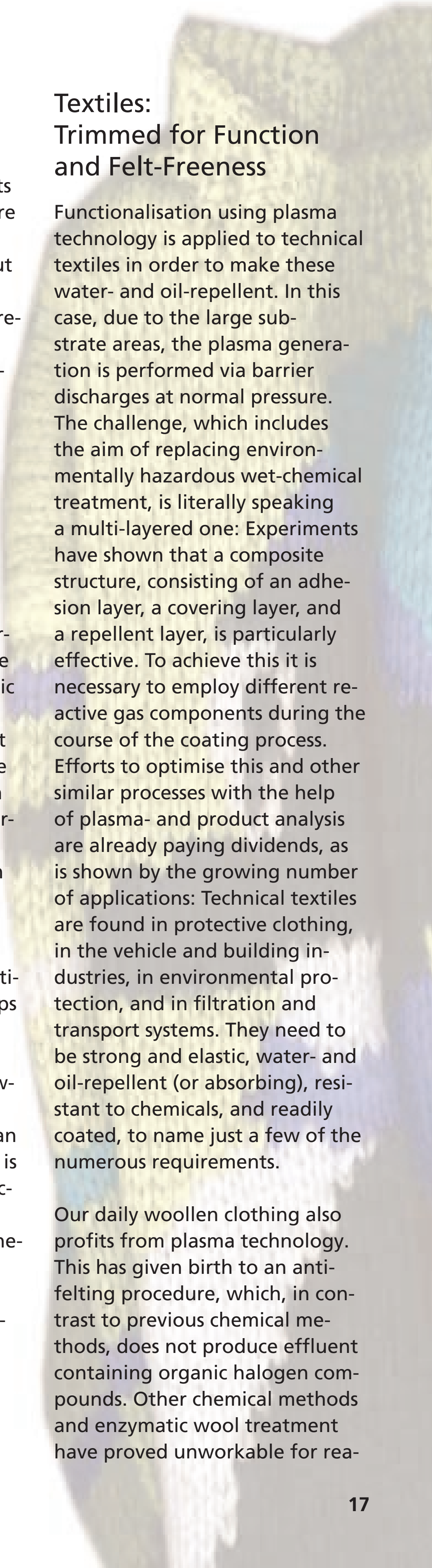
Typical objectives of surface activation are to make a surface more receptive for paint or to achieve better adhesion for the production of a sandwich structure. The ability to influence surfaces in this way results from the high energies of the electrons in a plasma, energies that are sufficient to disrupt chemical bonds. Corresponding plasma-assisted processes already play a significant economic role. For example, millions of car bumpers are plasma treated before they are painted. Another major area of application for plasma-activated products is in the packaging industry. Here they serve to increase the visual appeal, and hence sales. Without plasma treatment, printing on film and plastic packaging is barely possible, since the ink does not adhere properly. Food packaging benefits further from the fact that plasma treatment also destroys microorganisms.

Hand in hand with their activation, one can also perform the fine-scale cleaning of surfaces. Without resorting to environmentally hazardous chemicals, plasma treatment allows the surfaces of metal components to be freed of the last traces of organic substances. The fine and finest-scale cleaning stages are the last in a series of cleaning steps. Fine cleaning can be performed with a variety of plasmas. Layers of organic substances of 100 to 500 milligrams per square metre can be removed from surface areas themselves in the square-metre range, whilst the surface of the component is simultaneously activated for further processing steps such as painting.

When treating surfaces with low-temperature plasmas one can often even go a step further than simple activation. The next step is the functional activation or functionalisation of the surface. For example, the treatment of synthetic components with oxygen as the process gas leads to the pro duction on the surface of hydroxyl, carbonyl, and ester groups, i.e. chemically functional molecular groups that make such pretreated objects receptive for further surface processes.

Below: The preparation of synthetic materials for painting is of great economic importance. Below right: Combined surface cleaning and activation of a metal component in a corona discharge at atmospheric pressure

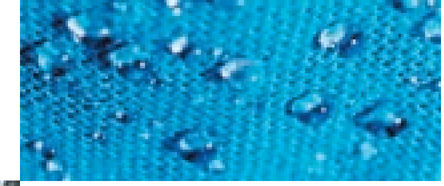


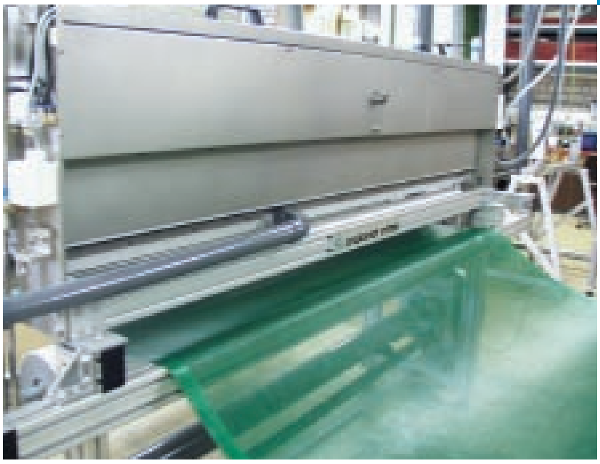


Textiles: Trimmed for Function and Felt-Freeness

Functionalisation using plasma technology is applied to technical textiles in order to make these water- and oil-repellent. In this case, due to the large substrate areas, the plasma generation is performed via barrier discharges at normal pressure. The challenge, which includes the aim of replacing environmentally hazardous wet-chemical treatment, is literally speaking a multi-layered one: Experiments have shown that a composite structure, consisting of an adhesion layer, a covering layer, and a repellent layer, is particularly effective. To achieve this it is necessary to employ different reactive gas components during the course of the coating process. Efforts to optimise this and other similar processes with the help of plasma- and product analysis are already paying dividends, as is shown by the growing number of applications: Technical textiles are found in protective clothing, in the vehicle and building industries, in environmental protection, and in filtration and transport systems. They need to be strong and elastic, water- and oil-repellent (or absorbing), resistant to chemicals, and readily coated, to name just a few of the numerous requirements.

Our daily woollen clothing also profits from plasma technology. This has given birth to an anti-felting procedure, which, in contrast to previous chemical methods, does not produce effluent containing organic halogen compounds. Other chemical methods and enzymatic wool treatment have proved unworkable for rea-





Above: Water- and oil-repellent textiles can be produced by plasma-based functional activation and coating.
Left: Finishing unit for technical textiles operating at atmospheric pressure.

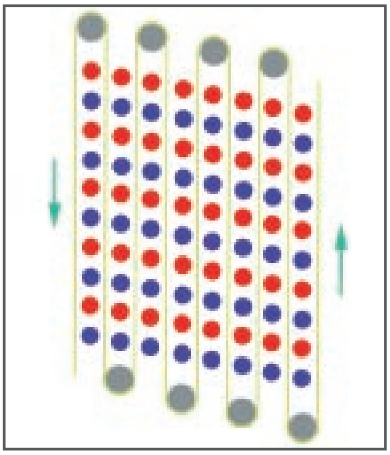
sons of cost or due to technical problems. Studies of plasma-technological wool treatment have been supported by the German Federal Ministry of Education and Research (BMBF: Bundesministerium für Bildung und Forschung). This support also has consequences for the textile industry: Companies can now extend their product range without the need to use environmentally hazardous processes. The upwards trend in sales of treated felt-free wool remains unbroken.

For wool producers, the plasma process, which is based on a barrier discharge at normal pressure, also has additional economic advantages: The protein material coats the wool fibre considerably less than in the chemical treatment. Weight loss, which was previously two percent of the valuable wool, is no longer a problem. In the further treatment steps, dying for example, the plasma-treated wool proves to be more resistant to protein loss than chemically treated fibres.

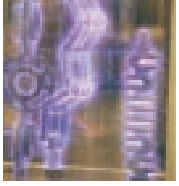
Among the demands placed on plasma technology by the textile industry is the use of low-pressure plasmas under vacuum conditions. This is important, for example, for the treatment of cellulose fibres in order to make these more readily wettable, e.g. for dying. The result: Treatment in a low-pressure oxygen plasma makes all cotton fabrics very easy to wet. The pretreatment steps that were previously necessary become superfluous and, furthermore, the time required for dying – and hence the total production time – is reduced. The colour quality of these cotton products is also improved.

A problem in developing these treatment procedures for textiles was the drying stage. Even dry cotton bales have a residual moisture content of one percent. This makes a step-by-step procedure under vacuum conditions unavoidable. In addition it is necessary to keep the gas discharges stable; for the large electrode areas needed for the textile web, the discharge has a tendency to flip over into a hot arc discharge. This problem was solved by distributing the gas discharge over more than a hundred separate electrodes. Another application of plasmas in weaving is in strengthening the warp threads, which are subjected to particular stress during the weaving process. For this purpose one uses a coating substance, which forms a protective polymer sheath around the yarn. Before the finishing of the fabric, however, the coating substance must be removed by washing and this, representing 40 to 60 percent of the total, is one of the main waste products of textile finishing.

A plasma treatment using a corona discharge with ambient air as the ‘process’ gas improves the adhesion between the coating substance and the fibres. This reduces the amount of coating substance, and likewise the amount of waste. In addition, a more uniform coating of the yarn is achieved, making it more robust. Hence, machine stops due to broken warp threads are also rarer.



Facility for the treatment of textile web in a low-pressure plasma. Diagram: Arrangement of alternate positive and negative electrodes used to achieve a large electrode area.



Hard Shells, Soft Centres

The wide range of plasma processes opens up a multitude of possibilities to exploit plasmas other than pure noble gas plasmas. Just by bringing in atmospheric nitrogen – a gas that under normal conditions is considered chemically inert – one can change the picture dramatically. In a plasma, the nitrogen molecule, consisting of two nitrogen atoms, breaks apart. The resulting radicals and reactive ions are able to participate in reactions with the surfaces of workpieces. This circumstance is intentionally exploited in the production of especially hard tools and components, such as drills, ball bearings and cogwheels. In this process, the surfaces and near-surface regions of the components are modified and one thus speaks of a **plasma-boundary procedure.** However, the strongest modification of surfaces by means of plasma is that achieved by coating; one also finds combinations of activation, functional activation and **coating** in a single plasma process.

With still other process gases one can coat surfaces to give them seemingly magic properties: for example, permanent shimmering colours, extreme hardness – not just as hard as steel, but as hard as diamond! – or gas impermeability. There is already a market and/or an enormous commercial potential for objects furnished with each of the above properties. Many of these procedures have been developed with the support of the BMBF.

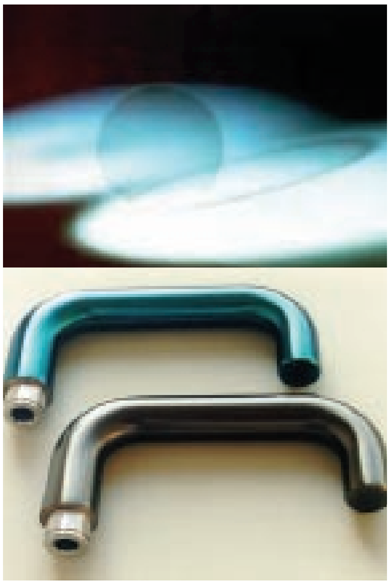
With a suitable coating it is possible to treat metals such as brass, which are otherwise susceptible to scratching and tarnishing. The results are door handles that retain their shine even after many years and, as a further option, can gleam in shimmering colours.

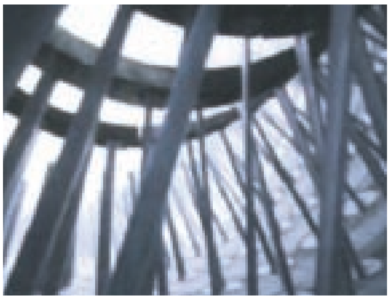
By using carbon containing reaction gases in a plasma another magic spell can be cast, one that is reminiscent of the philosopher's stone. Many alchemists sought after this stone, for it was believed that anything it touched would be turned to gold. Plasma can do even better: it can produce diamonds! However, the process is not quite so simple …

All the same, with plasma-assisted CVD procedures (CVD stands for chemical vapour deposition and means that chemically active gases are deposited on substrates) one has the capability to generate

To give the customer maximum satisfaction, it is essential to have packaging which can protect sensitive foodstuffs from going bad due to contact with the atmosphere. Here, too, plasma technology is promising to bring about a revolution: The PET market is currently growing at an annual rate of ten percent, in both the processing and the machine branches. Expressed in numbers, the year 2000 saw the production of about 120 billion **bottles made of the synthetic material polyethylene terephthalate (PET)**. Until now, these have mostly been used for bottling table water and other soft drinks. As a container for beer, PET was so far less suited – not only for reasons of taste. The problem is that PET allows too much oxygen to penetrate into the bottle and too much carbon dioxide to escape. This means that the beer quickly goes flat and begins to taste bad. However, a solution is in sight thanks to plasma technology. The first machines for coating freshly blown PET bottles are now in operation. One procedure makes use of amorphous carbon as an internal coating and is carried out in a low-pressure plasma with acetylene as the process gas. The barrier properties of PET are thereby improved thirty-fold for oxygen and seven-fold for carbon dioxide. The necessary thickness of the amorphous carbon layer is a mere 100 nanometres! Another procedure involves the deposition of a thin silicon oxide layer on the outside of the bottle. This enhances the barrier properties by roughly a factor of four. An advantage of this latter procedure is that the PET bottle remains as clear as glass, in contrast to the milky appearance of the carbon-coated bottle. Such coated PET bottles are becoming genuine competitors to the glass bottle. The commercial potential of these bottles is enormous – approximately 300 billion beer bottles are required per year! For the environment, this technology promises benefits too, for example, through the reduced fuel consumption for transporting the bottles. The BMBF is supporting work on the sterilization of synthetic bottles and packaging, also in conjunction with coatings.

Above: diamond wafers of 5 cm diameter and 0.3 mm thickness grown in a plasma. Below: door handles with carbon coating





Coating of the blades with a ceramic material improves turbine efficiency because such turbines, both in aeroplanes and in stationary installations, can be operated at higher temperatures.

diamond wafers of some centimetre radius and of millimetre thickness. These are used as particularly effective cooling ‘plates’, for example on microchips or in laser diodes. Diamond conducts heat five times better than copper but is electrically insulating. Diamond and diamond-like layers can also be deposited on the surfaces of work pieces for the purpose of reducing wear. This is useful, for example, in car manufacture and mechanical engineering. Having been coated, the components can be further processed, partially without requiring coolant and lubricant – a further BMBF-supported contribution to environmental protection. The coatings described here are not only extremely hard, but also very precisely controlled: Employed to coat razor blades they yield more effective yet gentle shaving.

An especially important gain for the environment, in absolute terms, is achieved by the use of plasma technology in the production of **coated architectural glass**. Without detracting from personal comfort, such glass allows huge savings in heating energy. Compared to normal window glass, coated panes reduce the heat loss in winter by up to 60 percent. For every square metre of treated window glass this amounts to a saving of 20 litres of oil each winter! Thus the thermally insulating glass produced in a single year leads to an annual saving of nearly a billion litres of oil; the associated reduction in the emission of the greenhouse gas carbon dioxide is two-and-a-half million tonnes per year.

The coated glass exploits a simple physical trick: When deposited as a thin film on glass panes, certain metals and oxides allow visible light to pass unhindered, but they reflect the longer wavelengths corresponding to thermal radiation. New technologies involving efficient large-area glass coating are yielding especially good results; they were developed, in part, with the support of the BMBF.

Investigations are currently in progress to test the suitability of photocatalysers for the cleaning of glass window panes. The glass is coated with very thin photocatalytically active layers using a plasma procedure. Other future developments will lead to windows in which the properties can be modified by electric, thermal or chemical activation. It is not inconceivable that windows will one day also be a source of electrical power.

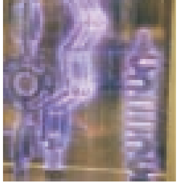
Car headlight reflectors, metallised by plasma technology and then, without breaking the vacuum, coated with a transparent protective polymer layer by introducing the appropriate process gas into the plasma.

More than Meets the Eye: Invisible Structures

The appearance of an object is determined by its surface. The surface is also important in questions relating to wettability and friction. If the surface contains structures of nanometre dimensions, properties emerge that are untypical of the normal material or supplementary to the normal properties. Plasma technology is now being used to commercially exploit such **nanostructuring**, allowing a wide cross section of the community to benefit from improved products.

A nanostructured system from nature, namely the eyes of mainly twilight- and night-flying butterflies and moths, provided a model for one such development. When light impinges on the interface between two media, reflection may occur due to the sudden change of refractive index. However, the presence of surface structures that are smaller than the wavelength of light produces instead a gradual change in the refractive index, for example at the interface between air and glass or another transparent plastic material. The eyes of many butterflies have such a surface structure, with an array of microscopic domes which improve the insects vision by reducing reflections.

For those who wear glasses, the question of reflection at the air–glass interface is also relevant. Antireflection optics have so far been achieved mainly by using layer systems that reduce reflection by exploiting interference effects. The eyes of butterflies point the way to an alternative means of producing reflection-free glasses using nanostructures. The structuring can be performed simply

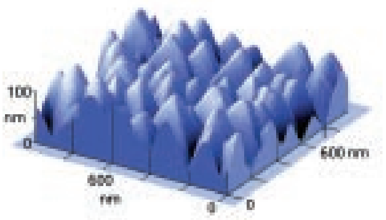


by using a stamp. This is an effective instrument with which a large number of individual surfaces can be rapidly structured. The problem of creating the stamp itself has been solved by plasma technology.

Plasmas have provided a tool with which thin nanostructured ceramic layers can be deposited onto a metal stamp, which in turn is used to transfer the nanostructure, e.g. onto Plexiglas. The formation of the ceramic nanostructure is a self-organising process; however, the plasma conditions must be carefully controlled so that the desired self-organisation can take place.

The result is an example of the frequently invisible effect of plasma technology: Plexiglas that has been treated in this way is particularly transparent with less than one percent of the incident light being reflected; here, too, the ‘butterfly eye’ has proved itself. A technical challenge for the further development is to control the plasma used to produce the stamp in such a way that three-dimensional forming tools such as rollers can also be uniformly coated.

A further application exploits the influence of surface structuring on the wettability of the surface. Plasma engineers have now established ways of modifying the wettability of glass surfaces at will: from readily wettable to water-repellent. But this requires more than meets the eye – more structure and more information. For water-repellent panes of glass one can use domes on the scale of a few tens of micrometres. Here, too, the model system is an invention of nature: With similar structures made of wax crystals the leaves of the lotus plant are protected from moisture and contamination. Perhaps windscreens of the future will use the same technique to make windscreen wipers redundant. Without streaking, the raindrops would simply form beads which fall from the glass.



The scanning force microscope reveals the structure of a ceramic surface, produced in a plasma by the deposition of the ceramic on a metal. Under appropriate conditions this hill structure is produced by self-organisation. Like the similarly structured butterfly’s eye, it suppresses light reflection.

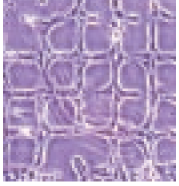
Plasmas are not only useful for depositing material on surfaces; they can also be used to remove material. In this case, one speaks of **plasma etching**. Procedures of this type can also be used to structure a surface, and are of immense importance in **chip manufacture**. Without plasma processes we would not have any of today’s high perfomance computers and memory chips! Plasmachemical processes have proven indispensable as a means of etching (and also vapour-coating) of wafer surfaces, since they enable significantly smaller structures to be produced than are possible with conventional wet-chemical processes.

Nanostructuring is not the only application of plasma etching. Relatively large-area structures, but ones demanding nanoscale precision, can also be formed with the help of corresponding procedures. An example is the aspherical lens. Such lenses are used, among other things, to avoid colour aberrations; when using normal lenses, further correcting lenses are required to deal with these, meaning, for example, that cameras require larger and heavier lens systems. Up until now, aspherical lenses have been produced with special coatings of a synthetic material in a complicated and expensive process. With support from the BMBF, researchers are investigating a method involving plasmachemical etching with high removal rates. The main element of the equipment is a microwave plasma-jet source. The aim of the research is to develop a process that allows low-cost manufacture of aspherical lenses, making high-quality images accessible to the mass market.

Scanning electron microscope image of a butterfly’s eye. Microdomes, each about 200 nanometres wide, help to give the insect reflection-free vision.

Direct Benefits to Man

Health is an especially important topic for all of us. What good are all the fine things in life if physical weaknesses prevent us from enjoying them? Plasma technology will play an increasingly important role in ensuring that individuals not only live to a greater age, but can also remain active for longer. The use of plasmas in medicine is leading to new diagnostic and therapeutic possibilities. The strain experienced by patients is often simultaneously reduced.



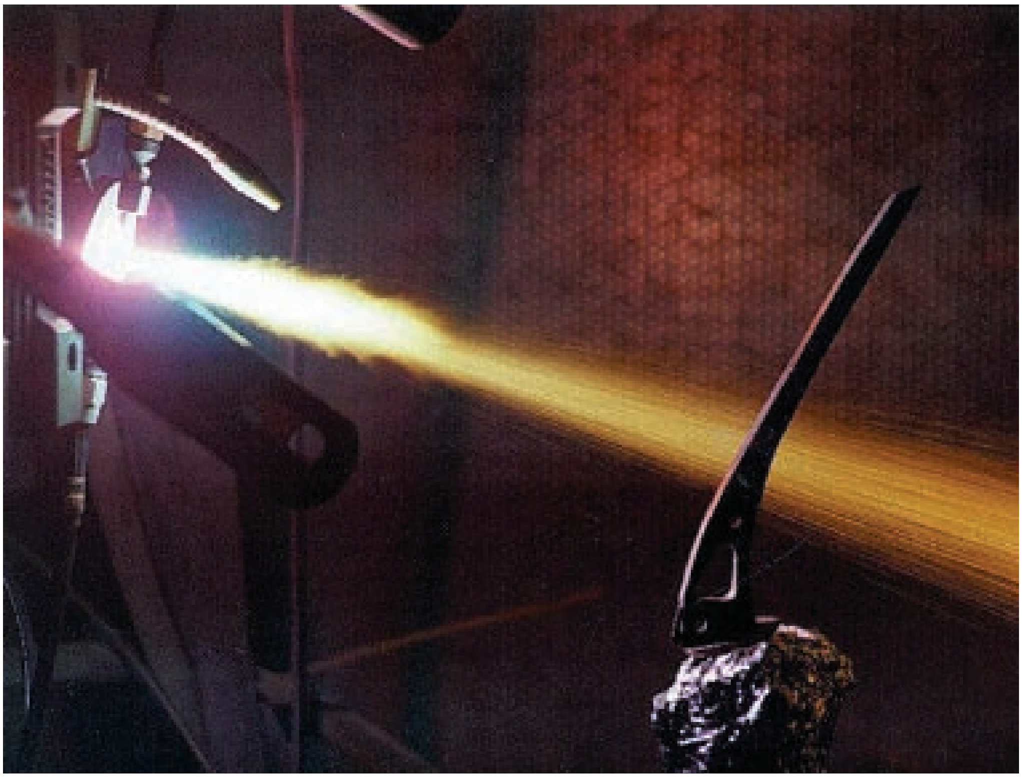
Joining and Protecting

Gradual Transitions Enhance Acceptance

It is not only car motors that run better when they are well oiled, or when the latest plasma coatings are used to reduce the friction. Movement of the human frame also needs lubrication. Usually this is taken care of by nature, but with advancing age it is possible for joints to suffer from the effects of wear and tear, in extreme cases leading to complete loss of mobility. Particularly susceptible are the hip joints, and thus artificial hip replacements have been available for a long time. But these have been further developed over the years, continually improving the long-term functioning of such prostheses so that repeat operations are less frequent. The previously described potential of plasma processes to modify surfaces already suggests that **medical applications** of this technology could also bring immense benefits.

Indeed, the ball and socket of artificial hip joints can be hardened using plasma processes. A special medical challenge, however, is the creation of a suitable join between the prosthesis and the bone. It is essential that the artificial joint remains reliably anchored in the bone, otherwise further operations are necessary to repair loosening joints.

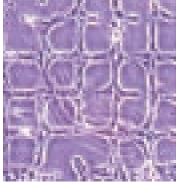
Novel coatings, some consisting of bone-like ceramics can be deposited with plasma technology to improve the rooting of the implant in the bone tissue. Via the use of bioactive coatings, it is possible to combine the advantages of a high-strength metal implant with the good **biocompatibility** of ceramic materials.



Artificial hip joint in the process of coating by atmospheric plasma spraying

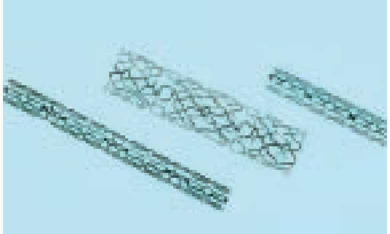
The **coating of implants** can be carried out in a variety of ways. For example, through the deposition of graded layers a continuous transition between the bioactive material and the weight-bearing prosthesis components can be achieved. This avoids or at least reduces the problem of insufficient layer adhesion that arises when there is a sudden jump between materials with differing mechanical properties. Also conceivable is a linear transition between bioactive layers and layers that disintegrate and are absorbed by the body's own tissue.

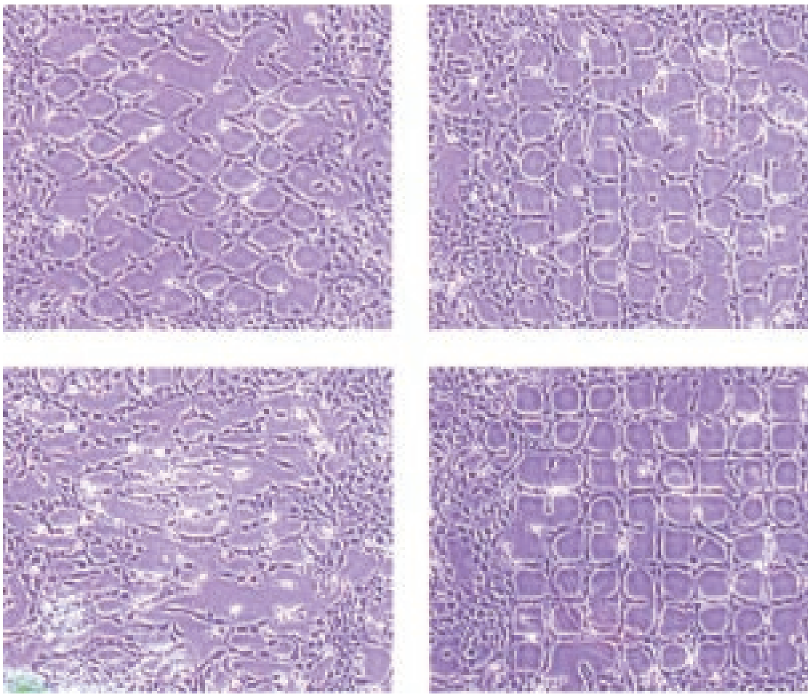
Coated hip replacements, however, are just one example of how plasma technology is being applied in medicine. The spectrum of plasma-supported applications ranges from these hip replacements, via artificial knee joints, heart valves and eye lenses, breast implants, tendon and ligament prostheses and false teeth to artificial blood vessels.



Joining and Protecting

Various types of stents





Micro-structured growth of mouse cells on polymer surfaces that have been chemically micro-structured with the help of plasma

Biomaterial with Tailored Adhesion

High-tech coatings make it possible to fulfil seemingly contradictory demands. This is clearly seen in the case of stents. These are cylindrical wire-mesh structures used for holding open arteries, thus sometimes avoiding the need for a heart bypass operation. The stent systems in use today occasionally give rise to complications due to the interaction of the material with the inner wall of the artery; this is responsible for the 35 to 40 percent risk of restenosis or reclosure of the artery. Using a plasma procedure, a carbon layer with diamond-like structure can be deposited on such stents. This is very smooth, hence preventing scratching of the arterial walls. At the same time, by matching the properties of the coating to the steel wire, the stent remains flexible enough to stretch the arteries. In fact, normal catheters can also be improved with the help of plasma technology: Their surfaces can be modified to make them adsorb less fibrinogen, which contributes to reducing the risk of thromboses.

Recently, plasma technology was successfully employed to minimise the build up of deposits (fouling) which impair the functioning of microfiltration membranes. In the first step plasma is used to functionalise the membrane for the uptake of suitable coatings. In laboratory tests with model substances (proteins), it was possible to reduce the membrane fouling by a factor of 10. At the same time, the selectivity of the membrane was increased from 60 to 95 percent. This will be of benefit not only for seawater desalination but also for separation processes in the food and pharmaceutical industries. Dialysis patients in particular should profit from a more reliable blood detoxification process.

Materials used as substrates for cell cultures can also be treated with plasmas so that they offer especially favourable conditions for the adhesion and growth of biological cells. This is particularly important for cell cultures that are intended for the growth of replacement tissue, such as skin or – looking further into the future – even replacement organs. Already in use are plasma-coated biosensors, which carry enzymes, and immunoassays with which it is possible to detect the presence of certain protein structures – an instrument for the diagnosis of pathogens in the blood.

The development of gentle plasmas for the **structuring of functionalised polymers** for use as biomaterials is supported by the BMBF, with a view to achieving the above-mentioned aims of cell growth and adhesion.

Plasma-treated knee prosthesis

Gentle but Tough on Microorganisms

Applications of plasma technology in the medical and health sector are not limited only to surface treatments. A further important area is sterilisation. Here, too, the use of plasma opens new horizons. An example is the **sterilisation** of dialysis-tubes in their packaging, a procedure that reduces the risk of infection for patients with kidney failure. The added advantage of the plasma treatment is that the same process used for sterilisation can also confer anticoagulant properties on the surface of the dialysis tubes. Since this reduces the likelihood of the formation of blood clots, the patients need smaller doses of anticoagulant drugs. They are thus less susceptible to high blood loss following injury.

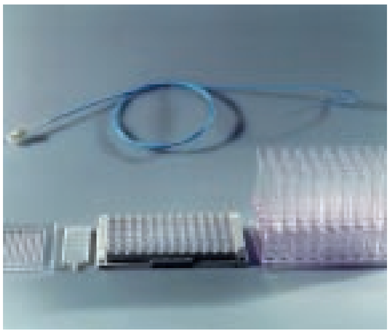
The fundamental importance of plasma sterilisation lies in its ability to sterilise heat-sensitive objects that cannot withstand hot steam. Until now these have been treated with gamma rays or chemicals. Here again, plasma technology can help to preserve the environment through its inherent sustainability with minimum consumption of materials. Sterilisation is achieved with the help of plasmas either by using plasma-generated UV light to kill bacteria, or by the direct effect of reactive gases. Let us look at a further example of how plasma sterilisation fulfils special requirements: Enzymatic biosensors are currently being developed for the continuous monitoring of the blood-sugar concentration of diabetes patients. One problem that had to be solved concerned their sterilisation, since they are implanted under the skin. However, the enzymes are so sensitive that conventional methods of sterilisation would destroy them. Plasma technology helped to solve this problem.

A further contribution to medical progress is made via the role of plasma technology in **pharmacy**. Of interest to the manufacturers of pharmaceuticals are the extremely smooth pressing tools that plasma helps to create for the production of tablets. These contribute to reducing the amount of spoilage during production. Furthermore, owing to the low surface energy of the plasma-treated tools, it is no longer necessary to employ a mould release agent, thus improving the quality of the tablets.

But even the efficacy of drugs can be improved using plasma technology and this, for example, can lead to more specific treatment with lower doses of medication, hence milder side effects. The basic mechanism for the conditioning of medicaments in plasmas involves the modification of minute particles of the compound – often of nanometre dimensions – in order to make them more readily absorbed. Furthermore, the particles can be prevented from disintegrating prematurely ensuring that they arrive intact at the location where they are needed.

Plasma applications in medicine go even further. For example, one may mention devices to fragment kidney stones by focussing destructive energy onto the stones in the form of an acoustic wavefront. A spark plasma is used as a switch for this process. Or one might think of the various light therapies, which are based on plasma-operated lamps.

Plasma-sterilised catheter; sterile sample holder

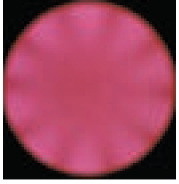


Plasma-coated tablet presses enable production without mould release agent

Gentle Power

Ions, radicals, electrons – these particles are not only present in plasmas, but are part and parcel of normal chemistry as well. Chemical reactions frequently involve interactions between these reactive species or electronically excited states of molecules. So it is not surprising that chemists are also trying to perform chemistry with plasmas, where reactive particles are present in 'unadulterated' form. Under mild overall conditions it is possible to drive reactions whose activation actually requires highly excited particles. And it is also possible to control these reactions by regulating plasma conditions such as the pulse parameters.

Pulses, in fact, are essential for many of the tasks addressed by plasma technology. A non-chemical example is the fragmentation of reinforced concrete in such a way that additives are cleanly separated out. For further materials processing tasks plasma technology offers a whole range of varieties which can be exactly tailored to the application at hand: drilling millions of holes per hour in circuit boards is just one example.



Cold Reactions

Process Gases Eager to Combine

The emergence of **plasma chemistry** can be traced back to the middle of the 19th century. In 1857 Werner von Siemens invented the ozoniser, a device for producing ozone in a corona discharge. In this, normal diatomic oxygen molecules react to produce ozone, a reactive gas whose molecules each contain three oxygen atoms. Almost one-and-a-half centuries later, the exact chemical processes that take place in this ancient device are still not fully discovered – a sign of the complexity of plasma-chemical processes, but also an indication of the opportunities that arise through the analysis and control of such processes.

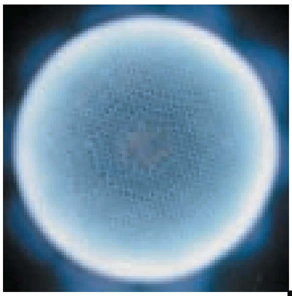
Examples of plasma-chemical processes have already been described in previous sections: Surface treatments including activation and fine cleaning, functionalization and coating, and the plasma boundary layer processes, are all based on chemical reactions. In the fine cleaning of metals, for example, plasma promotes the reaction between small amounts of residual organic substances, such as oils or fats, on the one hand, and oxygen on the other. Oxidation converts these substances into volatile compounds that can be pumped away. In the case of **activation**, a noble gas plasma acts on a polymeric substrate. The noble gases and their ions and electrons cause polymer bonds to break, thereby creating radicals on the surface that are able to participate in subsequent reactions; the surface is activated. The radicals can also react with one another, giving rise to an especially highly cross-linked surface layer.

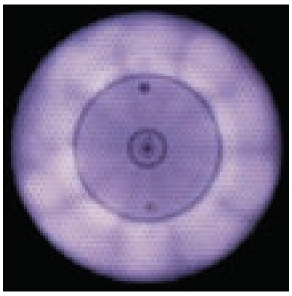
In the case of **functionalisation**, the process gases are not noble gases but typically oxygen, nitrogen or ammonia. Their fragments, generated in the plasma, penetrate into the surface between the polymer molecules and yield functional groups which can also participate in further chemical reactions. A possible future development is the plasma-chemical modification of polymers to provide plasma-assisted microstructures, which can be used as functional separation or carrier materials. The BMBF is sponsoring projects designed to elucidate these questions.

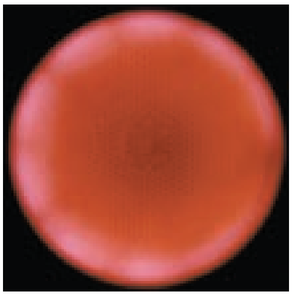
A common feature of activation and functionalisation is that in both cases the plasma gases are not themselves capable of polymerisation. If the plasma were to contains substances that polymerise – carbon, silicon or sulphur compounds, for example – the fragments generated in the plasma would react on the surface of the substrate forming a new polymer layer, one which would be highly cross linked and mainly amorphous structured.

Plasma chemistry, however, can do more than modify surfaces: it can also be used to **synthesise gaseous compounds** at atmospheric pressure. As in the case of solid substrates – although there only on the surface – collision processes between molecules and highly energetic electrons cause radicals to be created. By controlling the electron energies, by varying the effect of the plasma for pulsed plasmas, it is possible to specifically promote certain reactions and to suppress others, something that is not possible **with such precision** in normal aqueous chemistry.

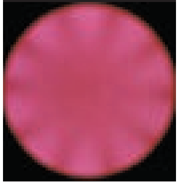
A particular motivation for plasma chemists is the development of alternatives to catalytic processes. Such processes have contributed a large part to the enormous success of industrial chemistry.



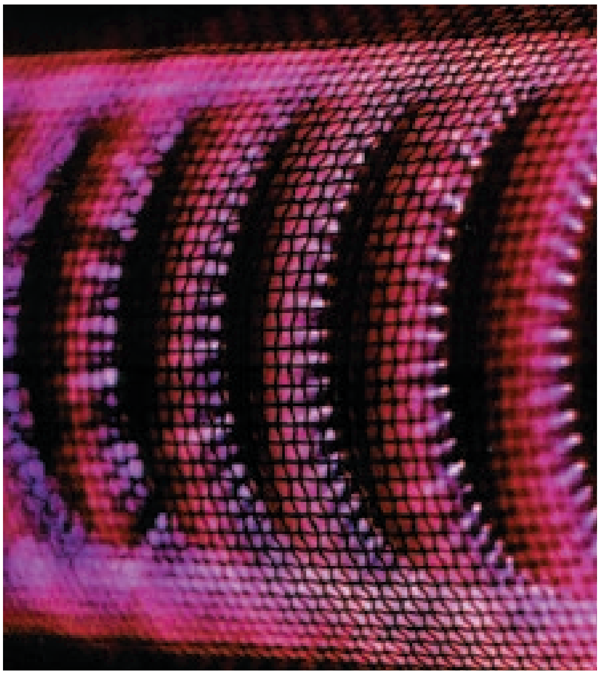




Microwave plasmas of various gases and under different pressures



Cold Reactions



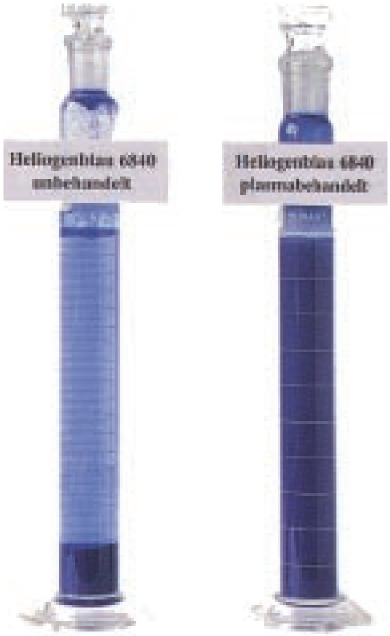
In this reactor gas-phase chemical reactions take place in non-thermal plasmas

Catalytic processes usually require a lot of space and frequently employ expensive catalysts; they are often carried out at high temperatures, and are sensitive to impurities (catalyst poisons). These disadvantages are the reason why plasma chemistry is so promising. An alternative effort in this area is investigating the use of plasma-chemical processes to polymerise colloidal systems which can then be employed in homogeneous catalysis. This research is also being supported by the BMBF.

Plasma reactions can be carried out over a wide range of temperatures, since they are initiated by high-energy electrons. They are hardly dependent on the gas temperature. They allow a faster throughput of matter than catalytic surface reactions, since the plasma technique initiates bulk reactions in gases, and these are less restricted by material transport processes. In conjunction with catalysts, plasmas are able to extend the application spectrum of the former, and also improve their efficiency. A possible field of application of plasma reactions is the conversion of hydrocarbons for the decentralized generation of hydrogen. Solutions to this challenge will have great potential, since one approach to the development of emission-free cars is to use fuel cells which generate electricity from the 'cold' reaction of hydrogen with oxygen. An uncontrolled reaction of hydrogen with oxygen is an explosion in which water is produced. Another possible use of such fuel cells is for a decentralised domestic power supply. Since natural gases contain large amounts of carbon oxides, plasmas could also be used in the exploitation of so far uneconomical sources. Likewise, the selective synthesis of long-chain hydrocarbons from methane is a challenge for plasma chemistry.

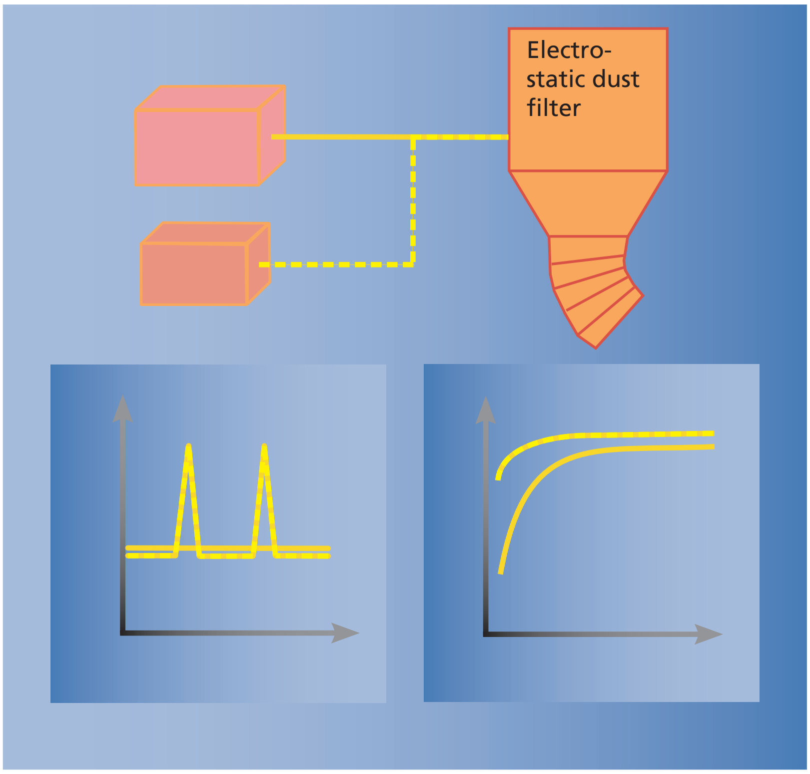
The **chemistry of pigments** is another area that is profiting from plasma technology. In the case of pigments the concepts of surface and bulk merge into one. The surface layer of atoms or molecules in a nanometre sized pigment particle represents a considerable fraction of the total number of atoms/molecules. The properties of the pigment are thus strongly influenced by the surface of the individual pigment particles; and surface reactions are one of the showpieces of plasma technology.

By means of plasma processes, some of which are still under development, it is possible, for example, to hydrophilize the pigment particles in paint. The trend today is towards water-based paints, for the sake of the environment. Organic paint pigments, however, are often non-polar. In a polar aqueous system they tend to clump together in large aggregates. However, if a powder of such pigments is introduced into a plasma with ammonia or oxygen as the process gas, amino- or hydroxy-groups are generated on the surface of the particles. This functionalisation increases the stability of their dispersion in water.



The weakly polar pigment copper phthalocyanine is poorly dispersible in water (left). Plasma treatment with oxygen is used to generate hydroxyl groups on the surface of the pigment particles, thereby increasing the polarity. The pigment then becomes readily dispersible in water (right).

Plasma chemistry can be successfully performed not only with non-thermal plasmas, but also with thermal plasmas. In comparison with the non-thermal procedure, one can now achieve particularly high material throughput either at atmospheric pressure or under elevated pressure. Such techniques are well suited to the dissociation of chemical compounds (plasma pyrolysis), for carrying out high-temperature reactions, and for the degassing or gasification of solid substances. The **thermal plasma chemistry** has its own history: It has been used since 1905 to produce nitrogen



The new plasma technology with pulsed electrostatic filters provides high dust separation rates and reduced energy consumption.

oxides, and since 1940 to produce acetylene.

Over and beyond the production related aspects, plasma technology also influences chemistry due to novel possibilities in **analytical chemistry**. This pertains to optical, spectroscopic and mass-spectroscopic methods. The last of these enable one to detect numerous different elements in a single sample in a matter of minutes. Optical methods are particularly simple and useful for low detection limits. The role of the plasma in these measurements is to excite the samples.

A well-established method these days is ICP spectroscopy (ICP stands for inductively coupled plasma). In mass spectroscopic and optical emission analysis devices of this type, the samples are excited by plasmas that draw their energy from the inductive transfer of electrical energy. Whereas mass-spectroscopic methods always require a high vacuum, the optical methods such as ICP-OES (optical emission spectroscopy) can be applied at atmospheric pressure as routine or screening procedures.

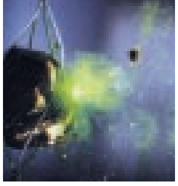
Pulsed Plasmas for Emission Control

Waste gases that would pollute the air can be made harmless by plasma treatment in large-scale installations. Some of such methods have already been established for a long time, for example, the electrostatic cleaning of flue gas. The aim is to achieve a drastic reduction in the quantities of aerosols emitted by industrial plants. Today, worldwide, more than 50 million tonnes of dust are released into the atmosphere. To combat this, Germany and other European countries have imposed strict rules concerning the decrease of gaseous emissions. Dust particles of sizes between one micrometre and several tens of micrometres are especially relevant for the climate, since they reflect sunlight; they are also injurious to health.

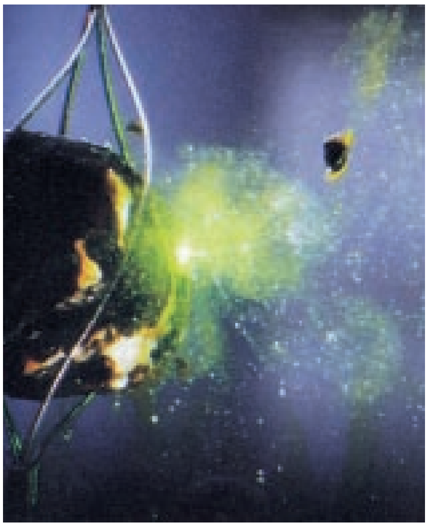
The electrostatic filters currently used for **cleaning flue gas**, cause the dust and smoke particles to become electrically charged in a corona discharge. They are then deflected out of the gas stream by electric fields into a collecting system. These filters are large installations: In power stations they may need to filter several 100000 cubic metres of gas per hour. Their efficiency today is somewhat higher than 98 percent.

Unfortunately, present-day electrostatic filters are inadequate for filtering out small particles in the single-digit micrometre region and below. Precisely these particles, however, pose a danger due to their ability to enter unhindered into the lungs. A higher charging of the particles to improve the separation is not possible because it would require impracticably strong electric fields in the filter. It is here that plasma technology steps in with the answer: pulses. With the latest high performance semiconductors it will in future be possible to achieve the necessary peak pulse power of 50 megawatts at pulse rates of 200 hertz. These **high-voltage pulses** are then superimposed on the plasmas in the particle filters. The dust particles under one micrometre are separated out. The short duration of the high-voltage pulse prevents the electrical breakdown of the filter.

This same principle is also suited for the construction of plasma-chemical reactors for, among other things, the conversion of fossil fuels or the chemical purification of emission gases. The BMBF is supporting both investigations of the plasma-catalytic oxidation of chlorinated hydrocarbons including the modelling of the fundamental processes. These will provide the basis for the construction of the corresponding plasma reactors.



Penetrating Properties



Pulsed Power

The capabilities of pulsed high-performance plasmas – also known as pulse power technology – paves the way for ecological problem solving in the field of **materials recycling**, for example in the fragmentation of concrete lumps. The principle behind such a process is the conversion of the electrical energy in a spark into a powerful acoustic pulse. With this technique, concrete blocks arising from demolition can be fragmented to yield a well-defined distribution of particle sizes. At the same time aggregate material can be selectively removed. Thus it is a promising method for recovering usable materials. Incidentally, the switching of the spark is also accomplished by plasma.

The principle of converting energy from a spark – itself also a plasma – into a powerful acoustic pulse can also be extended to other applications, for example the non-invasive fragmentation of kidney stones or gallstones. In the mining industry trials are underway to test the use of shock waves as an alternative to chemical explosives. The removal of unwanted deposits in pipes is further conceivable application of shock waves. The field of high-power pulses is necessarily related to plasmas: the high-power pulses need to be generated and switched. Typical switching voltages are in the range of 100 kilovolts; the currents that follow the switching operation can be as high as 100 kiloamperes. In pulsed industrial applications, the switches need to perform billions of times. Such requirements can often only be fulfilled by **plasma switches**; and here new developments are on the horizon.

Plasma switches are employed in power distribution; and here the electrical parameters have even higher values than those mentioned above. The examples show that plasma switches are a key component in pulse power technology.

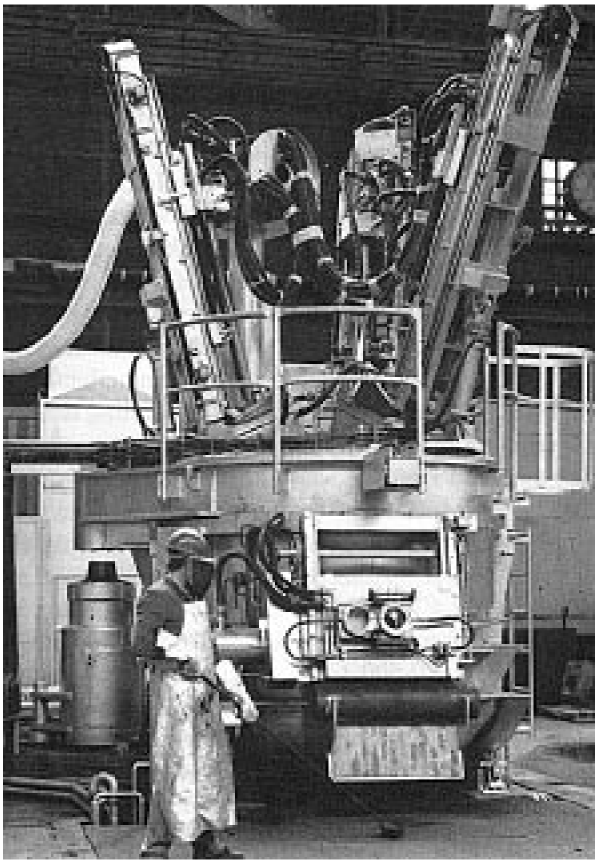
Plasmas as switches and plasmas as tools and as medium: these aspects come together in the form of pulsed discharge lasers such as the excimer and carbon-dioxide lasers. In these, the plasma serves as the switching medium in the switch for generating the pulse. In the laser itself the plasma is the medium for generating the radiation. And when such lasers are used in materials processing, the actual processing of the material takes place via the **laser-generated plasma**.

Such laser-induced plasmas have extremely high electron densities of up to 10^{19} per cubic centimetre. In materials processing, these plasmas are used for cutting, drilling and welding. In plasma chemistry they also play a role: Molecules with football and similar structures – fullerenes – can be produced in such plasmas. Curiously enough, laser-induced plasmas can, if the parameters are correctly chosen, themselves become lasing. In fact they radiate in the soft x-ray region as a result of the vast surplus of excited particles that they contain.

Gallstones are selectively shattered by powerful acoustic waves generated by laser-induced plasma pulses

Above: Aggregate that has been freed of cement by powerful acoustic waves; left: extracted reinforcements

Plasma switch for concrete fragmentation equipment



Experimental reactor for the combustion of filter dust

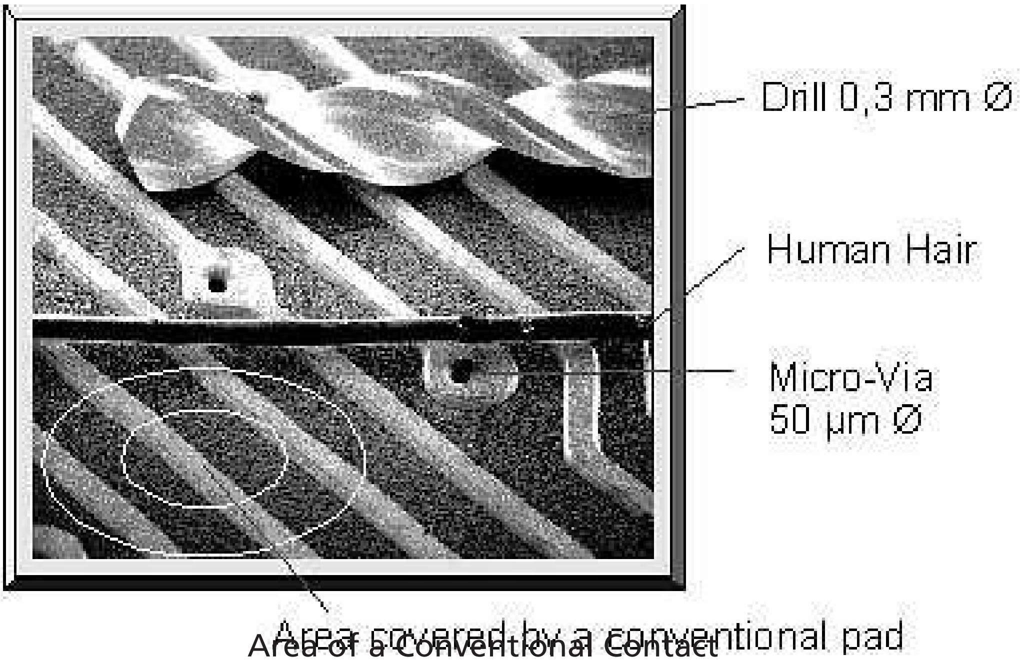
Melting and Drilling

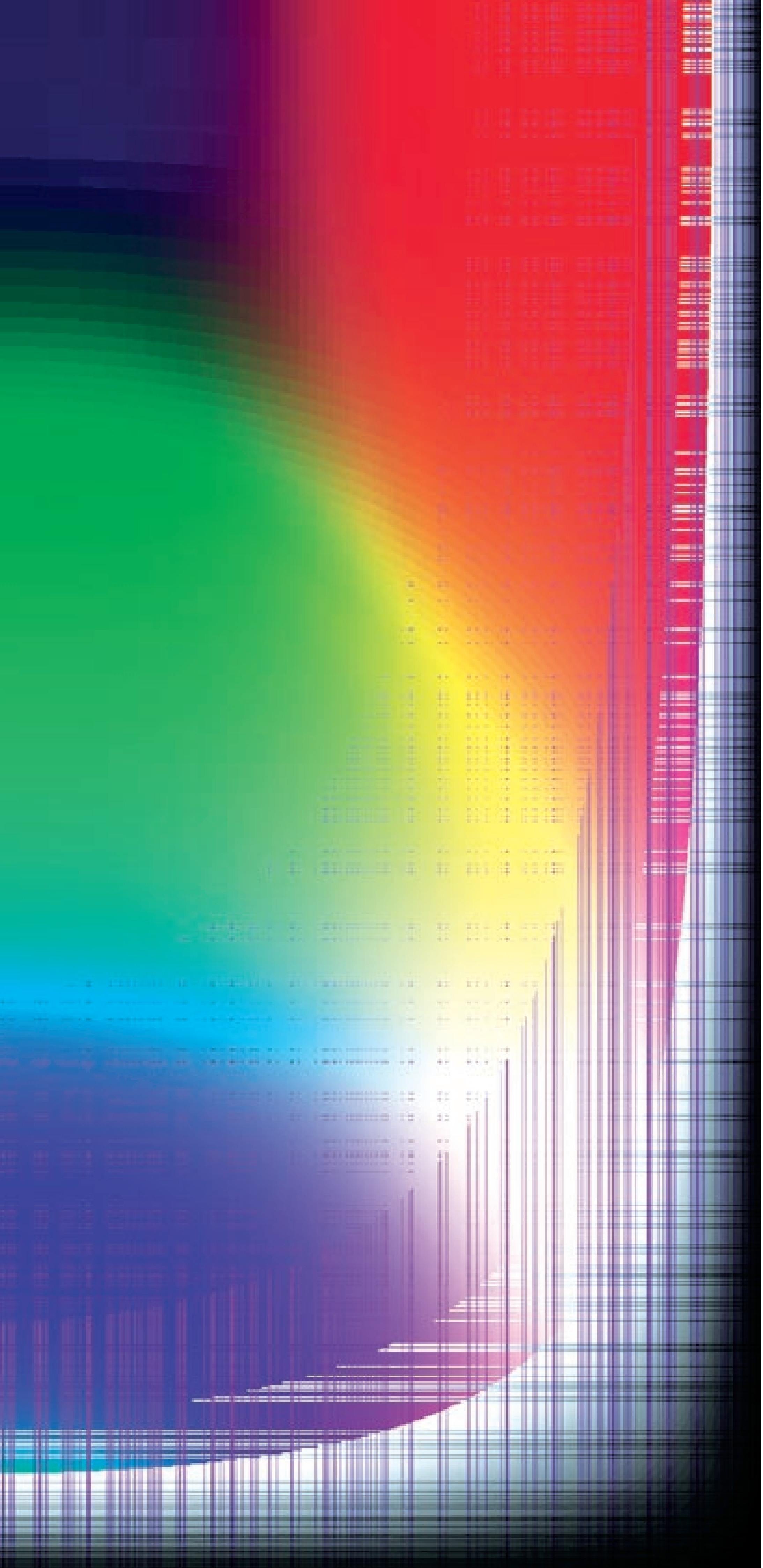
Pulsed plasmas have undoubtedly begun to conquer a wide range of industrial applications. One reason for this is the large variety of possible pulses, which provide many degrees of freedom, e.g. in manipulating reactions for solving plasma-chemical problems, and thus allow tailor-made solutions to be found. However, today's largest and most powerful industrial plasma plants, operating at a few tens of megawatts, are ones that run on a continuous basis. These are the plasma-melting plants, which are used primarily to melt steel scrap and to remelt alloyed steels and high-melting-point metals such as titanium, tantalum, molybdenum, or niobium. Plasma installations can also provide the controlled heating of steel melt necessary for optimised continuous casting.

Environmental protection also makes use of such high-power plasma burners: Rubbish incineration gives rise to large quantities of filter dust. This can be treated as special waste in a procedure that employs plasma burners. These melt the dusts and in the process thermally destroy dioxins and other poisonous compounds. Whereas untreated filter dusts have to be specially disposed of, the plasma-treated variety can be processed to yield a slag that is useful in the construction industry. To achieve this the melt is rapidly quenched; and heavy metals can be salvaged from the vapours.

Plasmas can cut, weld, melt and drill materials, even convert them into other materials, and sometimes they also provide the switching for the huge electric currents that are needed for these processing steps. So plasma is simply an energy tool in large-scale equipment and processing plants? Far from it, as demonstrated by a remarkable application from the electronics industry. In just an hour microplasmas etch millions of microscopic holes in printed circuit boards for the connection of components. They achieve dimensions that are ten times smaller than can be drilled with a microdrill. This makes an important contribution to further increasing the component density on such boards.

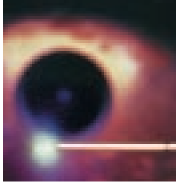
Plasmas etch millions of hair-sized holes in a circuit board in just one hour



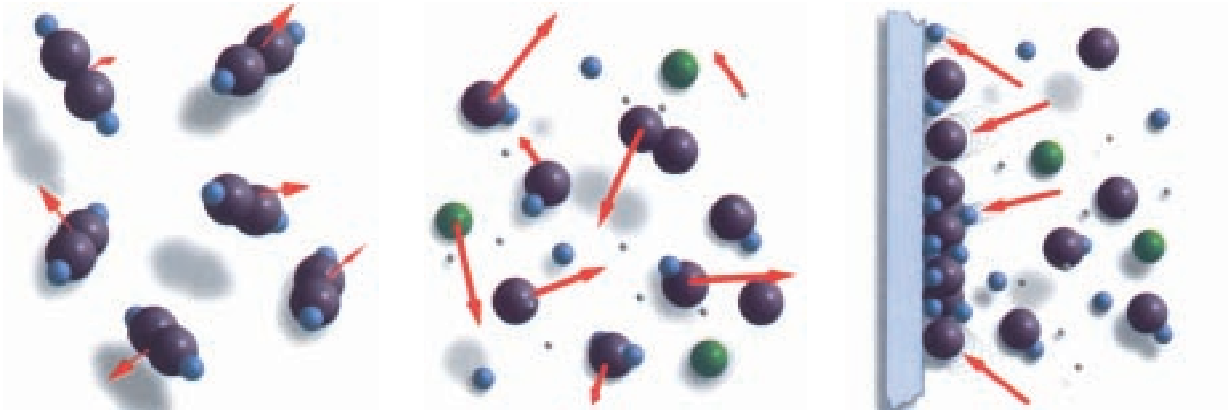


In the recent past, plasma technology has started to awaken from a long period of slumber thanks to significant new knowledge and technical progress, for example in power electronics. A large number of projects are in the development phase; many others have already generated products and production methods that are commercially available. But we are still at the beginning of the story.

The many degrees of freedom of the particles in a plasma, the large choice of process gases, the huge number of adjustable process parameters, and the innumerable possible reactor geometries area the reason why plasma technology has such a wide spectrum of applications. Product and process innovations, however, are not achieved without a considerable effort in the form of research and development (R & D) work. Processes have to be classified and the behaviour of the plasma understood so that it becomes predictable. Models and simulations of plasmas require reliable data from plasma diagnostics… These and more are the topics of ongoing research and development.



On Bonding and Boundaries



Acetylene molecules in the gaseous state (left) dissociate after acquiring sufficient energy into ions, electrons and radicals. These form a plasma (centre). When the particles of the plasma encounter a solid boundary (right) the result may be a sudden loss of energy; a layer of amorphous carbon is thereby deposited on the wall.

When Wall and Particles Interact

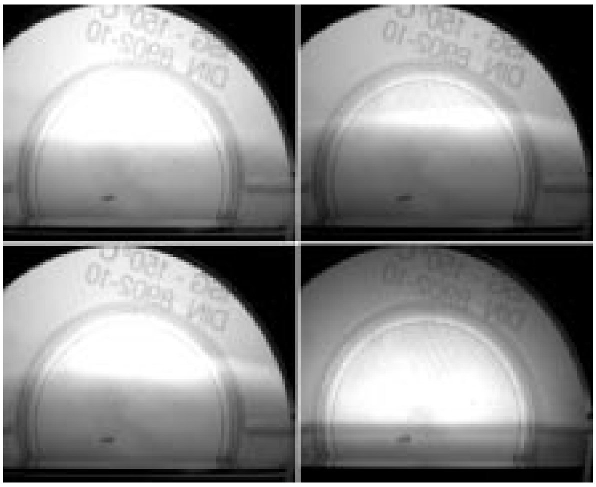
The systematic investigation and description of **low-temperature plasma physics** was for a long time neglected, as has been mentioned. The reason is that the particles, fields and currents in a plasma form a very complex system whose description is far from easy. The alternative trial and error approach has also been used, but with only limited success.

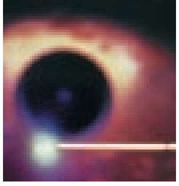
Probably the greatest challenge for researchers is to understand the interaction between low-temperature plasmas and the solid objects that border them. This interaction is characterised by drastic changes in the particle and energy states. The materials surrounding the plasma – whether these are the walls of the container or a work piece to be treated – influence the plasma in a wide variety of ways. For example, they mean that the plasma is never absolutely pure, because particles are constantly breaking free from the surfaces and entering the plasma.

Furthermore, different models are needed to describe the behaviour of the plasma in the vicinity of a solid body: Whereas 'free' plasma can, in thermal equilibrium, be largely characterised by methods that employ mean values, near to a solid virtually every particle behaves individually and requires its own calculation. Quite apart from that, the particles in the plasma itself exist in numerous different states, which must all be taken into account. Thus, 20 or 30 years ago, many problems of theoretical plasma physics could not even be described, let alone calculated. One always had to work with model zones, at best an incomplete description as experts now acknowledge. Only now is it possible, with the help of modern computers, to adequately model low-temperature plasma systems, provided they are not overly complex. Plasma models and simulations represent an important tool of the trade for the technical exploitation of plasmas.

A second challenge when it comes to controlling plasmas is their diagnostics. For a long time it was not possible to look closely at what was going on in a plasma and so there was no reliable numerical basis for calculations. Even now many data are missing, in particular data describing the transition of particles into different states and manifestations. The accuracy of the measurements needed to acquire such data impo-

The plasma boundary layer (shadowed area) depends on the discharge power and the pressure. A measurement of this layer thickness provides data about the plasma. In the images below, the pressure of the argon plasma varies from 0.005 to 0.01 millibar and the power from 10 to 50 watts.

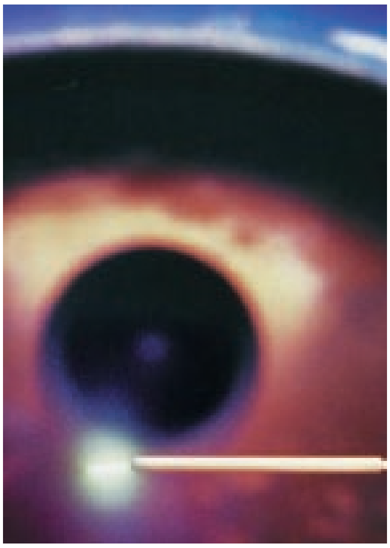




ses huge demands on the experimental apparatus. A magic word often heard when experts describe the latest developments in plasma technology is **pulse**. Planar surfaces can be best processed with likewise planar plasmas – if one knows how. However, unless special measures are taken, instabilities often lead discharges to abruptly change into another form. Discharge spikes arise and these are likely to damage the workpiece. This problem can be avoided by pulsing the plasma. Each instability requires a certain time to develop and a pulsed plasma leaves no time for the undesirable discharge forms to establish themselves.

Pulsed plasmas can do much more besides. In plasma chemistry they are used for the selective excitation of molecules. This is useful for applications in which certain molecule groups within chemical substances need to be selectively excited or removed. A prerequisite is that the plasma energy can be very precisely controlled. This is now achieved by varying the plasma energy in time. The plasma particles also have different lifetimes. By varying the pulse length and the pause between pulses one can establish different states of the plasma in which long- and short-lived particles are present in different concentrations. In many applications this can be used to maximise the yield of chemical reactions. Experts agree: in future time-varying plasmas will play an ever-greater role. Hand in hand with this development go increasing demands on plasma diagnostics, which is now required to be both time-resolved and position-sensitive. Likewise, plasma simulation and plasma source construction have to be adapted to the new challenge.

Fortunately, **plasma diagnostics** is itself making significant progress. In the past, plasma chemistry – which aims to study, describe and control the reactions of diverse particles in plasmas – was considered more akin to alchemy. One of the oldest, if not the oldest, plasma-diagnostic instrument is the Langmuir probe. This, in essence, is a wire that is used to determine the density of electrons or ions in a plasma. However, the results of such measurements should be treated with caution: Many plasma technological processes operate with gases that cause the formation of a thin non-conducting layer on the probe, thus leading to erroneous results.



Cylindrical Langmuir probe with ceramic shielding in a plasma. Before a measurement is made, a positive potential is applied to clean the probe. The resulting high current in the probe causes its tip to glow.

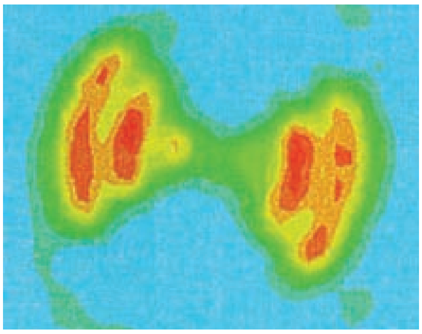
An alternative means of measuring electron densities in coating or reactive plasmas is the plasma oscillation method. Here a weak electron beam is injected into the plasma from a glow wire held at a negative potential. This beam excites a plasma oscillation, whose measurement contains information about the electron density.

Nonconformist but Existent

Modelling and simulation of plasmas make an important contribution to extending our understanding of plasma technological processes and also help to speed up the development of concepts for real systems. Simulations have profited from the fact that the mathematical foundations on which they are based have themselves made remarkable progress in recent years. Thus plasma simulations now exploit knowledge from – among other areas – chaos theory, synergetics, and evolutionary algorithms. Chaos theory and synergetics (in English-speaking countries the latter was subsumed in the endeavour known as **non-linear dynamics**) can help, for example, to explain rapidly occurring mode changes in plasmas. Evolutionary algorithms may be used to optimise the geometry of plasma sources.

Other branches of science have also profited from spin-offs from theoretical plasma research. An example is the existence diagram method, which is now enjoying significant success in meteorology. This method was originally developed in response to the challenge of describing plasma systems even when many of the data needed for the calculations are unknown.

Technological challenges that are especially important for future progress largely revolve around the **scaling-up of plasma processes**. This is necessary in order to transfer the results of fundamental studies of plasma processes, via applied research and pilot projects, to the level of industrial ex-



Example of a plasma tomogram

ploitation. Parameters that have to be scaled include size, time and pressure. If the dimensions of the equipment are increased, for example, it is necessary to correspondingly adjust the power rating and sometimes to re-optimise the geometry.

Changes in the time scale are usually sought with a view to reducing the processing time whilst maintaining the quality of the result. This is only possible with powerful, highly active plasmas.

Scaling of the pressure corresponds to an increase in the processing pressure, which in turn saves on equipment costs: today's plasma applications usually operate at low pressures and the necessary vacuum technology is not cheap. Thus the aim is to develop processes that can work at normal pressure. So far, however, attempts to perform plasma processing at atmospheric pressure have failed in all but a few cases, for example, the activation of surfaces.

Coating at atmospheric pressure represents a major problem for plasma technology. The reason can be found in the principles of gas dynamics: At atmospheric pressure, the mean free paths of the particles are very short; after travelling only a short distance they collide within the gas phase with other particles, thereby losing their reactivity or sticking together to form nanoscale dust particles.

However, the latter phenomenon, the formation of nanoparticles, can be exploited to advantage as a new means of creating nanomaterials. From **nanopowders**, it is possible to make materials that combine the properties of ceramics and metals. Nanopowders can be reliably produced in carefully controlled plasmas at high pressure.

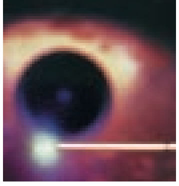
Laser diagnostics can measure the absolute number of atoms in different excited states in plasmas

Another area in which low-temperature plasma technology has great applications potential is in **remote plasma processes**. Here the aim is to use plasma to process highly sensitive materials, for which even the low thermal impact of standard low-temperature plasmas would be too high. Such materials may also be adversely affected by high-energy electrons which break molecular bonds. The trick with which researchers are trying to solve this problem is to decouple the plasma process from the plasma generation. Thus the workpiece is not actually in the plasma, but remote from it. The relevant process gas flows through the plasma, is excited by it, ionised, and dissociates, and then flows on into the remote region where the workpiece is located and where its treatment takes place.

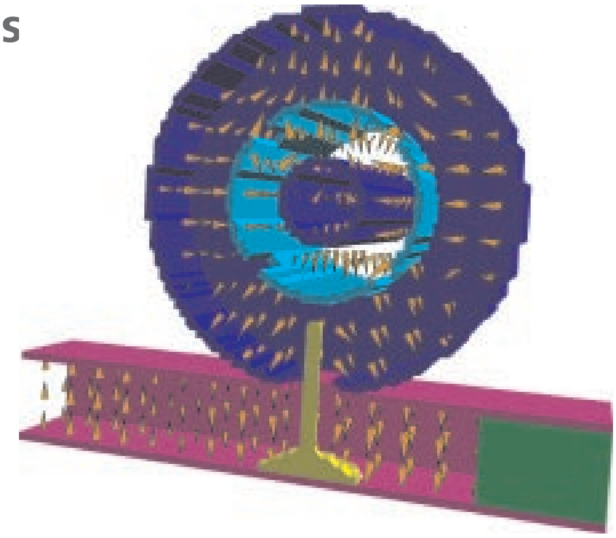
The data obtained in **plasma diagnostics**, can be used, either indirectly via simulations or directly via regulation of the system, to facilitate the manufacture of plasma-treated products of a uniformly high quality. Recently plasma diagnostics has particularly profited from progress in equipment technology – similar to the way in which simulations have benefited from advances in computer technology.

An important contribution here is played by spectroscopic methods, spurred on by recent developments in photodetection and laser technology. An example of the latter is laser-induced fluorescence (LIF) spectroscopy. Many industrially relevant plasma processes make use of molecular gases, and frequently gas mixtures. To examine these one requires a species-specific diagnostic tool, which is exactly what LIF offers. It allows excellent spatial and time resolution as well as a determination of the absolute particle densities in the electronic ground state, an important parameter for processing. In a pulsed oxygen plasma, for example, it is possible to use LIF to measure the dependence of the density of atomic oxygen on the pulse frequency and on the ratio of pulse duration to pulse interval.

Spectroscopic methods for the diagnostics of energetic states of



On Bonding and Boundaries



Calculated distribution of the electric field in a microwave plasma

atoms and molecules – for example, absorption spectroscopy with tuneable diode lasers or special methods of Raman spectroscopy – are supplemented by surface analytical tools. These include the scanning electron microscope, the atomic force microscope and Auger spectroscopy. Going beyond the examination of the plasma itself are tools for studying the plasma-chemical products, for example mass spectroscopy, gas chromatography and Fourier-transform infrared spectroscopy.

A promising current development is a method designed to produce cross-sectional images of the plasma. Analogous images, known as tomographs, are familiar in medicine. Plasma tomography provides information about the different atoms and molecules in a plasma, the different fragments (ions, radicals), their concentrations, and the temperature. It is also possible to extract three-dimensional parameter profiles; this is achieved simply by stacking a series of two-dimensional cross-sectional images.

Modern computers allow parameter fields to be calculated more or less in real time, so that the use of plasma tomography in process control should soon be feasible. This will allow specific parameter profiles to be selected and reproducibly regulated for a particular plasma process.

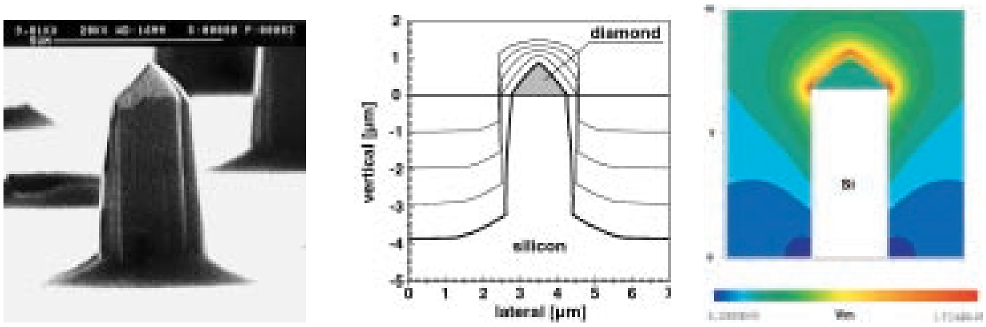
A current topic of fundamental research is the investigation of plasma crystals, regular arrangements of highly charged macroscopic particles in dust-bearing plasmas. Under the influence of their mutual repulsion and the surrounding electrical fields in a plasma, the particles settle into a crystal-like structure.

A Huge Task – Not only for Computers

The most important topics of further research and development in the field of plasma technology may be summarised as follows

- **Interactions of plasmas with materials**
  These play a key role in all technical surface processes.
- **Nonstationary, periodically or pulse-excited plasmas**
  These open the way to important new developments, since, in comparison to stationary systems, they provide a large number of additional control parameters.
- **Reaction kinetics of multi-component plasmas**
  Whether created in order to obtain a certain chemical process or simply due to impurities, these correspond to the true plasma state.
- **Reactive influences on the plasma**
  In addition to external experimental parameters, technical plasmas are also subject to reactive influences of the walls, electrodes and material samples.
- **Plasma control**
  Under well-defined conditions, technical plasmas must remain stable in order to ensure good product quality. This prerequisite is the task of control and regulation.
- **Modelling and simulation of plasmas**
  These support investigations aimed at obtaining a fundamental understanding of plasma-technological processes and also help in designing real systems.

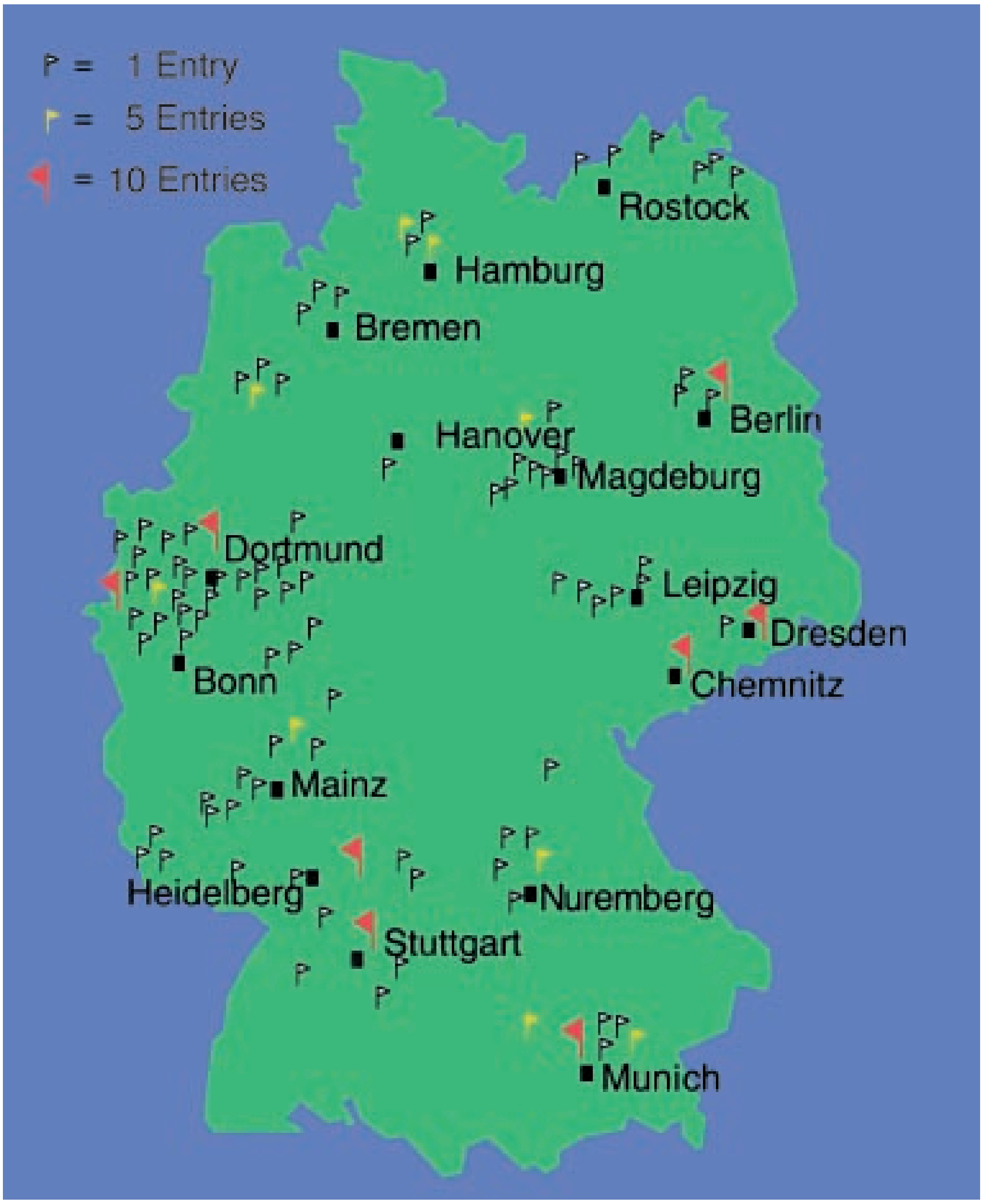
The tempestuous advances in computer technology have made a large contribution to progress in all the above areas. For example, when calculating the flow or the electric field – both important components of the plasma simulation – it is possible to formulate certain tasks in parallel. Then, on computers that contain a large number of processors (parallel computers), these quantities can be simultaneously calculated. Simulation methods also support the realization of field emitters, which can be produced, among other things, with plasma technology.



Below left: electron emitter for a flat display screen (diamond tip on a silicon column); centre: simulation of the diamond generation; right: field strength distribution

Plasma Technology in Germany

Opportunities for Technological Leadership



Today, many companies, universities and institutes in Germany are already working on aspects of plasma technology. The map on the right shows the results of a survey (1997) performed in conjunction with the production of the handbook ‘PlaTA – Plasma Technologies and Applications’. It is noticeable from the map that corresponding work is in progress in all parts of Germany. The flags indicate the number of entries in the above-mentioned handbook.

Funding by the BMBF has made an important contribution to strengthening the position of German companies in plasma technology and its applications. In the period from 1988 to 1996, support was focussed on the fields ‘thin film technology’ and ‘surfaces and coating technologies’, within which numerous projects investigating plasma-assisted coating procedures were sponsored. Since 1993, BMBF support of another major area ‘plasma technology’ has led to a significant extension of the applications of new plasma technologies in fields that go well beyond the above-mentioned surface and layer technologies. The projects that have been initiated to date are mainly industrial **cooperations** and have addressed the following topics:

- Pulsed plasmas and their applications
- Atmospheric pressure plasma sources
- Plasma switches for high-power pulse technology
- Electrode processes in discharge lamps and novel lamp fillings
- Plasma treatment of textiles
- Local high-speed plasma etching for finishing of optical surfaces
- Plasma technological methods for cleaning exhaust gases from combustion engines
- Plasma sterilisation of food packaging and thermolabile implants
- Plasma-chemical processes and their applications

Funding of Plasma Technology

The Federal Ministry for Education and Research supports **research projects in the field of plasma technology**. The main emphasis is on industrial cooperation projects, in which companies work together with universities and non-university research institutes.

The **aim of the funding** is to develop scientific and technical basics for innovative solutions, for example in life sciences, in environmental and medical technology, in electrical and vehicle engineering, and in materials processing.
The starting point is provided by the results of fundamental research, which have shown how complex low-temperature plasmas can be technically mastered. Emphasis is placed on resource-saving and environmentally friendly technologies and processes such as

- Novel plasma sources
- Efficient light generation
- Plasma-chemical methods for dry processing and for eliminating pollutants in gaseous emissions and aqueous waste
- Generation of new material properties by modification, conditioning, activation and functionalisation
- Cleaning and sterilisation
- Precision processing with plasmas
- Analysis

For questions relating to funding, please contact the **responsible organ of the BMBF**:

VDI-Technology Center
Physical Technologies

Graf-Recke-Str. 84
40239 Duesseldorf
Germany

Tel.: +49-211-6214-401
Fax: +49-0211-6214-484

http://www.vditz.de
http://www.plasma-net.de
e-mail: vditzpht@vdi.de

Depending on the exact question of interest, plasma technological challenges, besides receiving support in the area of ‘plasma technology’, can also be relevant for one of the other focal areas funded by the BMBF, for example:

- New materials
- Production technology
- Microsystem technology
- Nanotechnology
- Environment technology
- Energy technology
- Laser technology

Glossary

AC Alternating Current

State of **Aggregation** The physical state of matter as a solid, liquid, gas or plasma; determined by temperature and pressure, melting and boiling point.

Amino group Term describing the molecular group $-NH_2$

Amorphous materials Solids whose atoms are arranged in a disordered fashion with no crystal lattice, e.g. glasses, resins, or opal

Anode Positive electrode

Arc discharge Discharge created from a glow discharge at higher applied voltages. When the current density at the cathode increases sufficiently, the heated material begins to thermally emit electrons. There is virtually no upper limit on the size of the discharge currents; layers and zones disappear from the discharge.

Brush discharge Gas discharge which occurs predominantly at sharp points and edges of voltage bearing elements on account of the high electrical fields at these points.

Carbonyl group Term describing the molecular group =C=O

Catalysts Substances that accelerate chemical reactions or drive them in a particular direction. The catalyst itself is nor changed in the reaction.

Cathode Negative electrode

Chaos theory Mathematical theory for describing non-linear systems, which are characterised by apparently random yet deterministic behaviour and irregular structure formation. Small changes in initial conditions can lead to huge changes in the dynamics of such systems.

Clusters Aggregates of a few to a few thousand atoms that are either bound together or at least correlated in their motion.

Corona discharge Gas discharge in a strongly inhomogeneous electric field, i.e. especially at points and edges of a body which is held at a voltage. Only in the region of the strongest electric field does the collisional ionisation occur that is responsible for the light emission (in the form of a ‘light skin‘).

Cosmic radiation Radiation from space consisting of highly energetic nuclear particles, neutrinos and electromagnetic radiation. It can be detected, often after undergoing many transitions, deep inside the Earths‘s crust and in the ocean.

Dark discharge Also known as cold-electronic discharge. Non-self-sustaining discharge largely without photo-ionisation, for which only a low voltage is applied between the two electrodes. This type of discharge is applied in radiation dosimeters.

DC Direct current

ECR plasma sources (electron cyclotron resonance heating) Generated by microwaves with frequencies of up to more than 100 gigahertz and controlled by magnetic fields. They selectively transfer energy to the electrons in the plasma. ECR discharges are very pure and homogeneous.

Enzyme A biological catalyst: a high molecular weight protein that speeds up biochemical reactions

Ester groups Term describing molecular groups of the form –COOR

Etching Removal of solid material from a surface by means of chemicals, plasma, or electrolysis

Evolutionary algorithms Algorithms based on selection operations, of the type found in evolution (natural selection). They are well suited for finding solutions that better fulfil prescribed conditions than existing solutions. Thus they are optimisation tools.

Excimer Electronically excited molecular complex (excited dimer); extremely short-lived; emits an ultraviolet photon on decaying. Excimer complexes can contain two noble gas atoms (two argon, two krypton or two xenon atoms) or one noble gas and one halogen atom (fluorine or chlorine). Depending on the molecular complex, the excited state energy levels yield light of different wavelengths.

Fibrinogen Proteinagenous substance that plays an important role in blood clotting.

Fullerenes Substances composed of molecules in which carbon atoms form a closed three-dimensional framework surrounding a cavity.

A

Glossary

Functional group Molecular group that can substitute the hydrogen atom of another molecule. It endows a certain class of compounds with characteristic chemical and physical properties. Examples are the hydroxyl group of alcohols and the amino group of amines.

Glow discharge Gas discharge in low-pressure region with cold electrodes, currents in the range 0.1 mA to more than 100 mA and maintaining voltages of 70 V to several 100 V. Glow discharges develop from dark discharges when the current density is increased. A fully developed glow discharge displays a number of characteristic bright layers and dark spaces.

High frequency (hf) Term describing the range of frequencies of electromagnetic oscillations and alternating currents that lie between 10 kilohertz and 300 megahertz; these correspond to wavelengths between 30 kilometres and one metre.

Hydroxyl group Term describing the molecular group –OH

Immunoassay An immune test. An example is the fluoroimmunoassay: Pathenogenic substances (antigens) induce the production of antibodies that attach themselves to the antigen. Marking the antibodies with fluorescent substances allows the antigens can be tracked down.

Interference Phenomenon observed when two or more wave trains of similar wavelength are superposed. This effect is the basis for constructing filters that only transmit certain parts of the spectrum.

Kelvin Unit of temperature in the international system of units. Zero Kelvin corresponds to –273.16 degrees Celsius. A temperature difference of one degree Celsius corresponds to one Kelvin.

Lumen The unit of light flux in the international system of units.

Magnetron 1. Transmission tube for microwaves; 2. Equipment for generating plasmas for sputtering materials under the action of plasma; external magnetic fields optimise the sputtering rate for coating.

Microwaves Electromagnetic waves in the decimetre, centi-metre, and millimetre wavelength range with corresponding frequencies between 300 megahertz and 300 gigahertz. In the electromagnetic spectrum, they lie between radio waves and infrared radiation.

Non-linear dynamics Theory of dynamical systems whose equations of motion are non-linear (for example, the motion of a three-body system under the action of gravity).

Ozone Gas whose molecules each consist of three oxygen atoms. Toxic at room temperature.

Plasma The fourth state of matter, consisting of ions, electrons and neutral particles.

Polar light A luminous phenomenon observed at night over the polar regions. The light is generated when the path of corpuscular solar radiation passes through the Earth’s atmosphere at heights between 70 and 1000 kilometres.

Radical Atom or molecule with an unpaired electron. Typically very reactive and inclined to react with one another (recombination). Such reactions frequently generate new radicals so that a chain reaction may be initiated.

Radionuclide Radioactive atomic nucleus that can transform into a different nuclide by radioactive decay.

Sputtering Dispersion of materials by bombardment with ions.

Synergetics Cooperation of individual parts of a system leading to the formation of spatial, temporal or functional structures. Synergetic phenomena may occur in both deterministic and random processes.

Thrombosis A narrowing or closing of the blood vessels caused by a blood clot.

Wafer A thin disk made from a single crystal of a semiconducting material. With a diameter of up to 30 centimetres, a single wafer can accommodate hundreds or even thousands of integrated circuits.

Sources of Photographs and Illustrations

ANTEC GmbH, Kelkheim Germany (19)

Arbeitsgemeinschaft Plasmaphysik APP, Bochum (8 [2x], 11)

Aurion Anlagentechnik GmbH, Seligenstadt (7)

Balzers and Leybold Holding, Hanau (20)

BASF AG, Ludwigshafen (28)

Dyconex AG, Zurich, Switzerland (31)

Forschungszentrum für Mikrostrukturtechnik FMT, Wuppertal (5 [2x], 11, 27 [5x], 28, 33, 34 [2x], 36 [5x])

Fraunhofer Institut Schicht- und Oberflächentechnik IST, Braunschweig (19, 25)

Fraunhofer Institut Werkstoffmechanik IWM, Freiburg (21 [2x])

Friedrich-Alexander-Universität Erlangen-Nürnberg, Physikalisches Institut I (30)

FZM GmbH, Flöha/Sachsen (18, 20)

Helms, Thomas, Berlin (6)

Heraeus Noblelight GmbH, Kleinostheim (14)

Humboldt-Universität Berlin, Institut für Physik (15 [2x])

Institut für Niedertemperatur-Plasmaphysik INP, Greifswald (4, 23, 24 [5x], 35 [2x])

Institut für Textil- und Verfahrenstechnik ITV, Denkendorf (18)

Kickuth, Rolf (4, 5 [2x], 6, 7, 8, 9, 10 [2x], 13, 16 [2x], 17, 18 [after FZM], 21, 22 [with FMT], 26, 29 [after Siemens], 32, 37 [2, after PlaTA Handbuch Plasmatechnologien und -anwendungen, Raabe, Stuttgart], 38)

Laser- und Medizin-Technologie gGmbH, Berlin (5, 30)

Mannesmann AG, Dusseldorf (11)

Messe München AG (4, 17, 19, 21)

Osram GmbH, Munich (4, 12, 13, 14 [2x], 16)

Otto-von-Guericke-Universität Magdeburg, Institut für Allgemeine Elektrotechnik und Leistungselektronik (30 [2x])

PHYTIS International GmbH, Dreieich (24)

PLASMA-finish GmbH, Schwedt/Oder (25)

RWTH Aachen, Lehr- und Forschungsgebiet Werkstoffwissenschaften (23, 25)

Sidel Groupe, Octeville-sur-mer, France (33 [3x])

Siemens AG, Erlangen (28)

SOFTAL electronic Eric Blumenfeld GmbH & Co. KG, Hamburg (11)

Springer-Verlag, Heidelberg (9)

Thyssen Krupp AG, Duesseldorf (31)

Tigres Dr. Gerstenberg GmbH, Hamburg (17)

Universität Greifswald, Institut für Physik (33 [4x])

Federal Ministry
of Education
and Research

bmb+f

This brochure is distributed free of charge. It is not meant for commercial distribution. Political parties, candidates or their assistants are not allowed to use this brochure during electoral campaigns for campaigning purposes. This shall apply to federal, regional and local elections, and to election of members of the European Parliament. More specifically, distributing this brochure at electoral rallies and information stands of politi-cal parties, as well as inserting, impressing or labelling party-political information or advertising media shall constitute an abuse. It shall also be prohibited to pass on this brochure to third parties for campaigning purposes.

Irrespective of when, via what channel and in what number a recipient has obtained this brochure, it must not be used – even if there are no impending elections – in a way which could be interpreted as a bias on the part of the German Federal Govern-ment in favour of specific political groups.

BMBF PUBLIK