THE FUNDAMENTALS OF LOW-TEMPERATURE PLASMA TECHNOLOGY
The fundamentals of low-temperature plasma technology

In the following, the term plasma is understood simply to mean a wholly or partially ionised gas /1,2/.

The predominant proportion of the material is in this form, frequently also referred to as the "fourth state of matter" /3/. In technical terms, plasmas can generally be produced by the application of a sufficiently high level of energy, e.g. in the form of arcs, glow discharges, lasers, flames or shock waves /4/.

The individual types of particles in the plasma, i.e. ions, electrons and neutral particles (in the form of atoms, molecules and radicals), can be grouped in accordance with different temperatures /5/. Depending on the relationship of the temperature of the electrons (Te) to that of the ions (Ti) and the neutral particles (Tn), a distinction can be made between two types of plasmas with different chemical properties, i.e.

a) Te substantially higher than Ti and Tn:
At low pressures up to a few hundred Pa, the free path length of the electrons when accelerated by an external electrical field is relatively great and the number of impacts with other particles, in which energy is transferred, is relatively small. In this case, the temperature of the electrons can range from a few tens of thousands to 100,000 K, while the temperature of the ions and neutral particles remains relatively low at between a few hundred and 1000 K. This condition is therefore described as "low pressure", "low temperature" or "unbalanced" plasma. Technically speaking, it is usually produced by electrical glow discharges, while in nature it exists in the form of e.g. interstellar material or the earth's ionosphere.

b) Te approximately the same as Ti and Tn:
At higher pressures and levels of energy, the temperatures reach the same level, due to the greater frequency of impacts. These so-called "high temperature" or "balanced" plasmas are usually produced by means of an arc or in plasma torches or, in extreme cases, by nuclear fusion. The temperature of the gas particles lies within the magnitude of a few thousand to 10,000 K or, in the case of nuclear fusion, around 100 million K. Suns constitute natural high temperature plasmas.

As a rule, high temperature plasmas are too drastic in their effect to be used for the treatment of sensitive surfaces (an interesting exception is presented by the process described in bibliographical reference /6/). For this reason, this article will be confined to low temperature plasma - and will generally be referred to simply as "plasma".
2.1 Processes occurring in low temperature plasma

As a consequence of cosmic radiation and the radiation from radioactive isotopes in the chamber walls, a certain number of ions and free electrons are always present in the gas chamber of the reactor. These charge carriers are accelerated by the application of an electrical field. In plasma technology, both DC voltages and greater or lesser high frequency voltages in the kHz, MHz (RF) or GHz (microwave) range are used, depending on the application concerned.

Given sufficient free path length (obtained with an appropriately low pressure) and voltage, the more readily mobile electrons are able to absorb sufficient energy to ionise gas particles on impact. The electrons thus released are, for their part, accelerated in the field and rendered capable of ionisation. In this way, the number of charge carriers increases, the discharge current rapidly accumulates in turn and the discharge "ignites", producing the characteristic luminous phenomenon.

A steady state develops very rapidly in which as many charged carriers are generated as are destroyed by recombination. The average level of electron energy produced is between 1 and 10 eV (1 eV corresponds to 96.5 kJ/mol or 23.05 kcal/mol). Electrons with an energy of 1 eV can be assigned to a temperature of 7733 K or 11,600 K, depending on definition. By electron impact, gas particles can be excited to rotate, oscillate and absorb electrons. In this connection, metastable, electronically excited particles, which are unable to radiate their excitation energy, are of particular interest. These energies, some of which are high, are transferred in collisions with other gas particles or surfaces to the impacted substance. Fast-moving electrons with energies above 9 eV produce the ionisation of the gas particles.

The electron energies produced are finally sufficient to disintegrate any chemical bond. As a result, molecular gases are fragmented, up to a certain percentage, into atoms or multi-atomic radicals.

Depending on the state of excitation of the gas particles, the low-temperature plasma ("glow discharge") emits a light spectrum with components in the infrared, visible and UV ranges. The luminous phenomenon is characteristic of the process and delivers valuable signals for process detection and monitoring. The radiation emitted from the plasma - particularly its UV content - gives rise to photochemical reactions /7/. By contrast with normal photochemistry, which is limited to wavelengths in excess of 180 nm through the absorption of quartz or air, a highly energy-rich radiation of short wavelengths ("vacuum UV") occurs in low-pressure plasma. By this means, reactions are able to take place which are unknown in conventional photochemistry.
2.2 Processes occurring on the surface of treated parts

Bodies exposed to the plasma, e.g. the reactor wall or treated parts, do not remain unaffected by the process occurring in the gaseous phase. The neutral particles, electrons, ions and photons thus produced initiate a series of physical and chemical processes on the the surface, i.e.

a) On impact, neutral particles transfer (slight) kinetic and, if multi-atomic, also rotation and oscillation energy to the solid body, although this merely contributes to its becoming heated. With additional activation, moreover, chemical reactions with the surface can be achieved. Radicals may recombine on the surface, whereby the binding energy of the respective, enclosed bond is released at a level of a few eV. In addition, radicals can also react chemically with the surface of the solid body, e.g. by combination with radical points. This mechanism is of particular importance to practical applications (plasma degreasing, plasma activation, plasma coating).

Metastable, excited neutral particles whose lifespan is sufficiently prolonged to survive the gaseous phase, release high (in some cases) excitation energy, e.g. in the case of argon, around 11 eV. The effect of energy levels of this magnitude has not yet been fully explained, but it is believed that chemical reactions and the desorption of particles are induced in this way.

b) The electrons produced give rise to the desorption and disassociation of adsorbed molecules. In addition, it is believed that numerous chemical reactions are triggered off by electron bombardment. By virtue of their low inertia, the free electrons are considerably more mobile than the ions, with the result that more electrons hit the surfaces exposed to the plasma, per unit of time, than (mostly positive) ions. In consequence, the surfaces become negatively charged relative to the plasma, in so far as the charge cannot be conducted to earth, e.g. in the case of insulating workpieces ("floating potential").

c) Given this potential difference, positively charged ions are accelerated onto the negatively charged surface. In this process, they absorb, inter alia, sufficient kinetic energy (ranging from a few eV to a few hundred eV in the case of special systems for ion etching) to expel some particles (atoms, clusters or fragments of molecules, sometimes in ionised form) from the surface coating affected. The threshold energy for this process, known as "sputtering", typically lies around 15-30 eV under bombardment with argon ions. On impact with negatively charged surfaces, the (positive) ions are neutralised and the ionisation energy thus released - if appropriate, also the energy from electronically excited states - is transferred to the solid body.
This energy, which in the case of Ar+ and N2+ typically exceeds 15 eV, is frequently high enough to release secondary electrons from the surface of the solid body, through Auger neutralisation, which increase the degree of ionisation of the plasma. It has been possible to demonstrate that chemical reactions on surfaces can be markedly accelerated by bombardment with ions /10/.

d) The UV radiation from plasma is very high in energy. An Ar plasma, for example, exhibits two highly intensive emission lines at 105 nm (= 1,130 kJ or 270 kcal per mol). By means of electron spin resonance (ESR), it has been found that radical points in considerable concentrations can be produced through plasma UV radiation in polymers and glass /11, 12/. The surface cross-linking of polymers by means of plasma can largely be attributed to the effect of plasma radiation. The penetration depth of plasma UV radiation is markedly greater, by some μm, than the effective depth achieved by the processes described under a) to c) above. In contrast to these, the radiation produced in plasma polymerisation not only affects the direct development of the polymer films but also the depth of the deposited coating, which can lead to e.g. further cross-linking. The visible proportion of plasma radiation is generally absorbed only to a limited extent, while the infrared content merely leads to heating.

The use of low-temperature plasmas in industrial technologies

So far, "cold" plasmas have been most widely used in the production of electronic components, particularly in the field of microelectronics. Thus, for example, the fine structures of the most highly integrated circuits are routinely etched by plasma processes and the photo-resist mask subsequently also removed with plasma. Finally, even insulating or passivating coatings are being increasingly applied to the chip by means of plasma deposition. In reverse, circuits can be re-encapsulated and etched for the purpose of defect analysis. Plasma processes are used in the production of printed circuit boards to clean contacts, while in solar technology they are used for the deposition of amorphous silicon.

Still in its infancy, but increasingly gaining favour, is the use of plasmas for high-performance cleaning operations without CFCs, and, last but not least, the pretreatment of metal and plastic components to improve adherence prior to painting, printing and the application of foam and flock coatings and adhesives.