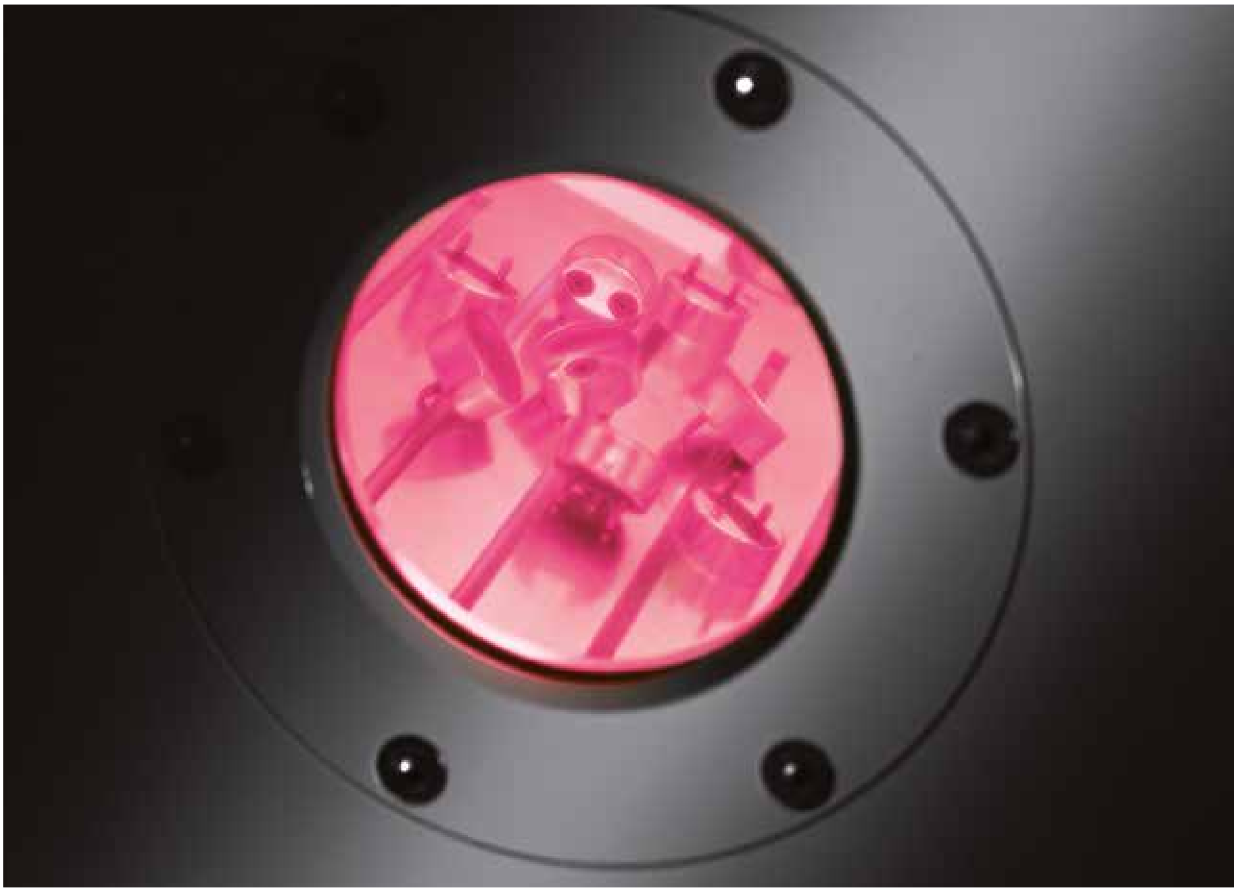
Systems for surface treatment with low-pressure plasma



Plasma technology

Contents

Systems for low-pressure plasma surface treatment

View into the reaction chamber of a low-pressure plasma system during a cleaning process

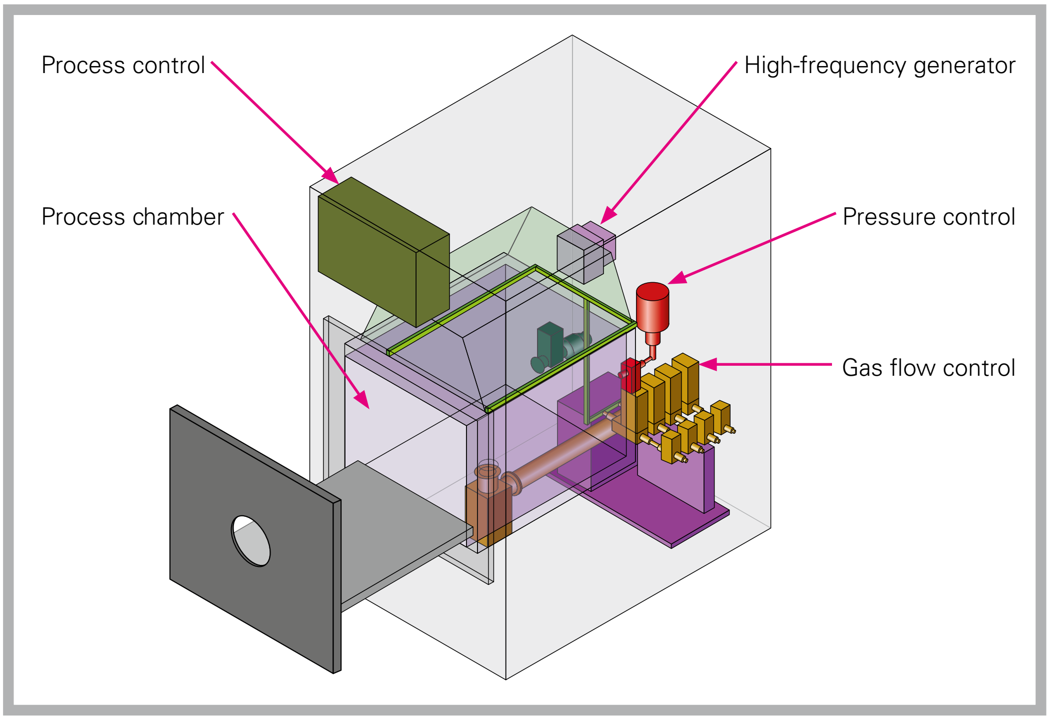
PINK GmbH Thermosysteme – founded by Friedrich Pink – is located in Wertheim/Main and has about 100 employees now. The product range includes low-pressure plasma systems for surface treatment, systems for vacuum-supported soldering, sintering systems as well as systems for drying and processing technology.

In the past years, the family business PINK has grown steadily and successfully due to continuous product improvements and consequent customer orientation.

PINK operates internationally with a network of sectoral agencies in all major markets and is a worldwide supplier of customized plants and systems. Well-known technology and research companies rely on the high-quality and innovative products of the company.

PINK is the suitable partner for high-quality and customized low-pressure plasma systems of any size and varieties of equipment configurations. PINK produces stand-alone units, reel-to-reel units as well as inline systems.

Schematic structure of a low-pressure plasma system



The gentle power of the fourth aggregate state

Plasmas known from nature: lightning and northern lights.

Matter changes its form of appearance at specific temperatures. Generally, solid, liquid and gaseous aggregate states are known. However, there is another state – the plasma. Plasma is the ionized form of a gas and is also named as "fourth aggregate state". The difference between neutral gas and plasma is the significantly higher electrical conductivity and chemical reactivity.

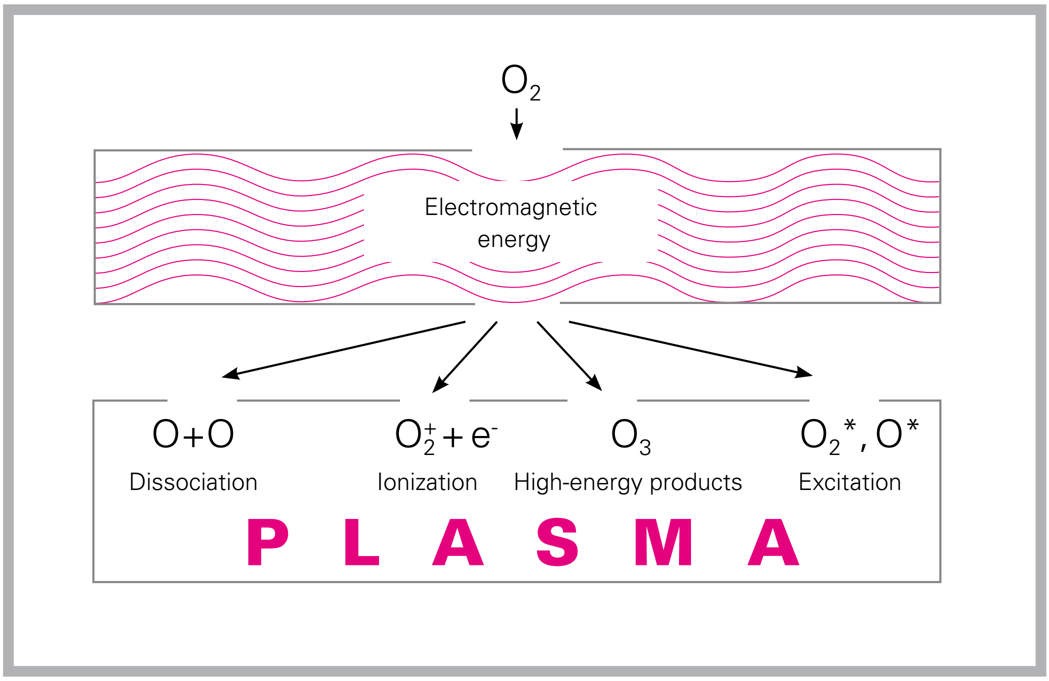
Samples for naturally occurring plasmas are lightning, northern lights or sun. However, in our everyday lives we also encounter plasma in the form of fluorescent lamps, low-energy lamps or television.

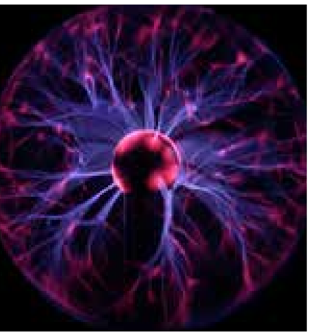
Low-pressure plasma: energy without heat

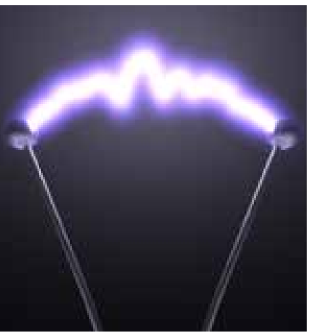
At atmospheric pressure, plasma is hot – as in flames and arc discharges.

If pressure is reduced to around 100 Pa (1 mbar), plasma can be formed and sustained even at room temperature. It is therefore also known as cold plasma or non-thermal plasma. However, the energy of the electrons corresponds to a temperature of several 1,000 K – forming a highly reactive medium. It enables both effective and gentle treatment of polymers and other temperature-sensitive materials.

The principle of low-pressure plasma







Artificially produced plasmas are e.g. the plasma lamp and the electric arc in welding technology.

The efficient method for best results

Wide range of application

Low-pressure plasma is produced by electromagnetic fields. The induced chemical reactions and physical effects depend on the respective gas and excitation frequency used for plasma formation.

The used gas, for instance, determines if the respective plasma is an oxidizing or reducing medium or neither of them (neutral).

Neutral plasmas

Neutral plasma forms e.g. if a noble gas like argon is used. The major effect of neutral plasma is physical: Contaminants are removed by a bombardment with heavy ions (sputtering). Low excitation frequencies (kHz range) will boost this effect significantly as ions will gain much more velocity before they impact onto the surface. As fast and heavy ions transfer heat to the surfaces they collide with, this method is limited to suitable materials and surfaces.

Reactive plasmas

Reactive plasmas are formed from gases like oxygen, hydrogen or fluorocarbons. The oxidizing, reducing or functionalizing effects originate from the ions and radicals present in plasma which readily react with the substrate material or the topping contaminant. After plasma treatment, surfaces are activated, passivated or particularly clean, respectively.

An especially high excitation frequency (GHz) promotes such reactions as it results in a high ion density in the plasma phase and therefore maximizes reactivity. Simultaneously, ion energies remain low, so sputter effects and heat load are minimized or not incurred at all.

Eco-friendly and efficient

Such procedures of the low-pressure plasma technology are not only extremely efficient, but also ecologically neutral and economically useful because usually no polluting waste products and no disposal costs incur therefore.

Exemplary low-pressure plasma treatment effects

- Removal of organic residues
- Activation by means of oxidation of polymer chains
- Coating by means of polymerisation of suitable monomers
- Removal of disturbing oxide layers by reduction
- Etching by the use of aggressive gases and reaction conditions

Varying process gases and excitation frequencies, there is a broad selection of possible plasma effects. Verification of the desired plasma effect on the actual substrate should never be skipped as thorough process development may be necessary. PINK warrants its developed processes and therefore safeguards customer's investments in PINK equipment.

Plasma properties regarding different excitation frequencies

	Low frequency (LF) 40 kHz	Radio frequency (RF) 13.56 MHz	Microwave (MW) 2.45 GHz
Plasma density	Low	Medium	High
Heat load	High	Medium	Low
Sputtering	Considerable	Medium	Low

Individual modification or activation of surfaces

A hydrophobic polymer surface prior a treatment with low-pressure plasma.

The same surface has hydrophilic properties after plasma treatment.

With the activation in low-pressure plasma, the surface tension increases and O-functional groups are incorporated into the PE surfaces. This improves bonding of the imprint.

Bonding improvement on polymers

The surfaces of countless industry-relevant plastics such as polyolefins (PE, PP, EPDM or PTFE) are nonpolar so they cannot be adequately wetted by paints, printing inks or adhesives. Bio-organic materials or metals are also often very difficult to coat or only with the aid of costly, specialized polymer products.

With the aid of low-pressure plasma technology, it is possible to simply and efficiently obtain an activation or chemical modification of polymer surfaces. In numerous industrial applications, this process has already proven itself in terms of improved polymer processing properties (bonding, printing, painting, etc.).

Areas of application

- Automotive and automotive component industry
- Medical technology
- Electronic industry
- Electrical engineering
- Chip card production
- Plastics processing
- R&D

Plasma activation – for excellent bonding properties in adhesive applications

In order to achieve adhesion between surfaces of unpolar plastics and adhesives, lacquers, paints, etc., polar groups must be created on the surfaces. This results in an increase of the interfacial energies and therefore in an increase in affinity.

If this, in addition, results in the formation of covalent chemical bonds between the substrate and the adhesive or coating, particularly good adhesion properties can be expected. Under such circumstances, the bond only breaks under high mechanical loads. It will not break at the interface but within the bonding components.

With low-pressure plasma technology, polar functional groups can be integrated into the surface of plastics. Depending on the gas applied, these may include oxygen groups such as –OH or nitrogen groups such as $–NH_2$. This effect is limited to the surfaces themselves. The polymer bulk material is unaffected.

In medical technology, numerous plastic components are plasma treated in order to achieve improved hydrophilic properties on surfaces of microtiter plates, syringe hubs, etc.

Long-term behavior of plasma-activated surfaces

Plasma activation produces covalent chemical bonds between oxygen and carbon atoms allowing interactions between the substrate surface and the coating material because of their polarity. Such chemical bonds are stable over time and there is no degradation under normal storage conditions. However, storage stability is influenced by the following factors:

- Subsequent contamination from outside
- Subsequent contamination from inside
- Physical processes in the material

Contamination from outside

Subsequent contamination from outside may occur due to improper storage or handling: Contact with contaminated objects or hands, dirty atmosphere in the storage room, transfer of volatile material components of the packaging material.

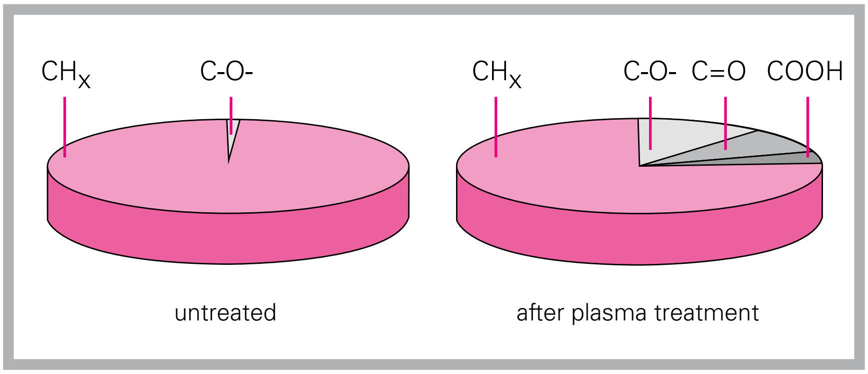
Contamination from inside

Today, many plastics are optimized for special properties by means of aggregates: plasticizers, UV stabilizers, coloring agents, fire-resistant substances, and many others. Such aggregates often are not chemically bonded within the plastic matrix and are mobile within the material therefore. After activation, such straying small molucules cause a masking of the active surface. This might happen even very quickly.

Physical deactivation

Directly after activation, all functional groups responsible for the activity are oriented towards the interface of the material. Over time, a statistic distribution of this orientation is achieved by means of rotations along the polymer chains around chemical single bonds. The groups are randomly oriented then and only a small part is available for interaction with the environment. Heat accelerates such processes because heat increases the mobility of the polymer chains.

ESCA analysis of a polypropylene surface



Composition of a plastic surface (PP) before and after oxygen plasma treatment.

Storage effects

Activation at proper storage and handling may outlast several months especially in simple plastics without additives (like polypropylene). Proper storage means a storage preventing contamination from the outside at max. room temperature. However, a slight reduction of the surface tension always has to be expected but it is not necessarily relevant for the results.

In all other cases, a renewed cleaning/activation to revive the surface is normally non-critical. However, reliable statements only can be made after appropriate tests.

Ultrapure surface cleaning

Clean and reliable method

Surface cleaning plays an important role in industry for improvement of coating adhesion.

Conventional cleaning methods have their specific limits and, following wet-chemical cleaning, traces of detergent or solvent are still found on the surface and are not completely removed even after thorough rinsing and drying.

However, low-pressure plasma cleaning results in surfaces free of organic contamination. Treatment cycles of just a few minutes give outstanding results with no surface residues.

The excellent crack penetration of low-pressure plasma is advantageous. This means that even intricately formed parts are perfectly cleaned since the gas also penetrates into small gaps that liquids cannot reach.

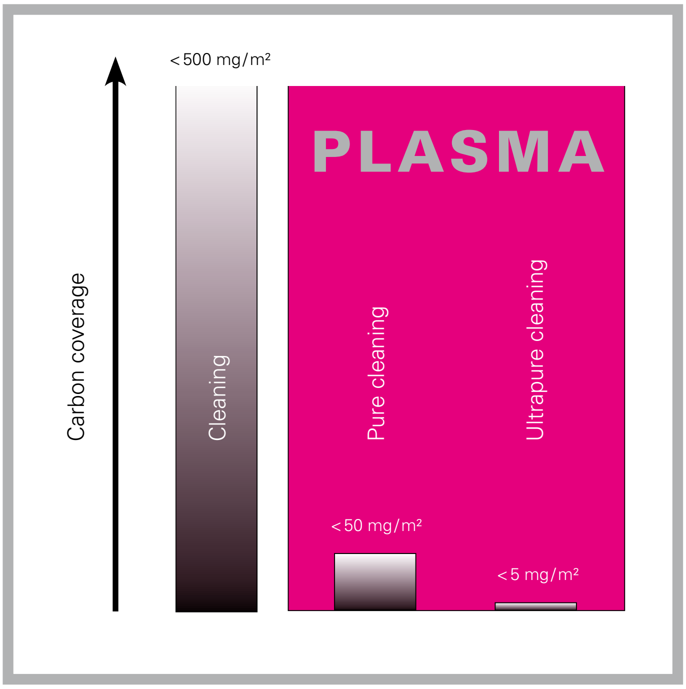
The decisive factor in the plasma cleaning process is the formation of gaseous and hence volatile products that can be removed from the sample chamber without any problems. The plasma components react with the organic contamination and degrade it to water and carbon dioxide at room temperature:

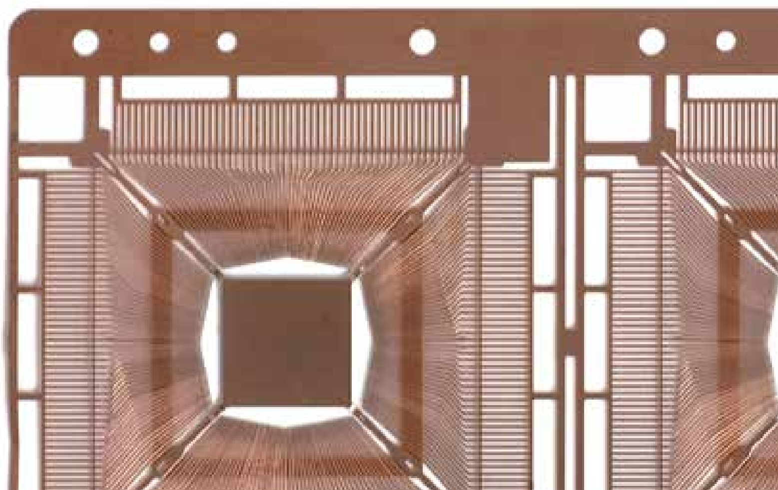
$$(\text{-}CH_2\text{-}CH_2\text{-})_n + 3n\ O_2 \rightarrow 2n\ CO_2 + 2n\ H_2O$$

Advantages of plasma cleaning

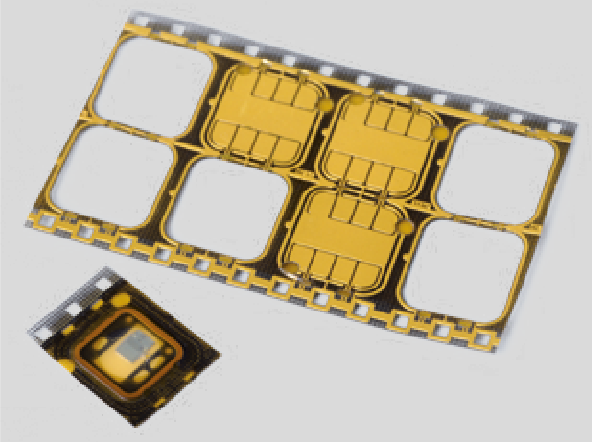
- Extremely clean surfaces (ultrapure cleaning)
- Low treatment temperature
- High crack penetration
- No downstream drying necessary
- No detergent residues
- No waste disposal costs
- Low operating costs
- Eco-friendly process

Cleaning categories





Cleaning in low-pressure plasma significantly improves the bondability of this leadframe.



Areas of application

- Optical industry
- Microelectronics
- Chip card production
- Electrical engineering
- Glassware industry
- Metalworking industry
- Watch industry

Production integration options

Intelligent automation engineering allows plasma systems to be integrated into production lines.

Selecting suitable pump systems allows evacuation times to be reduced to such a degree that cycle frequencies can be matched to application requirements. In addition, modularly designed systems allow a quick and flexible respond to production expansions.

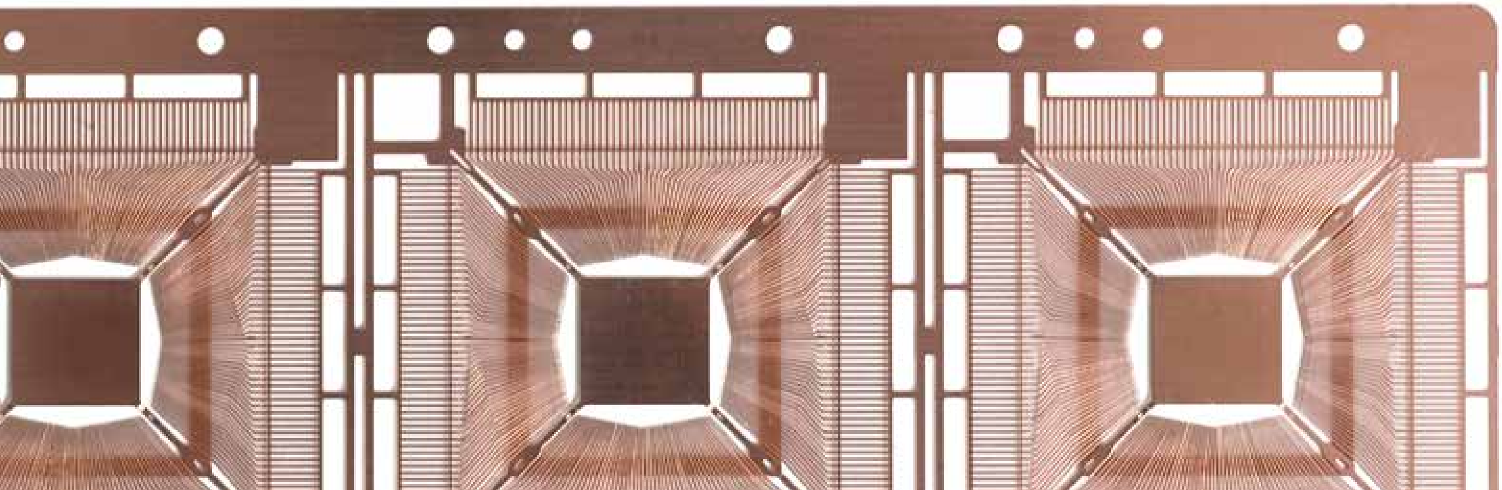
Suitable materials for low-pressure plasma cleaning

All vacuum-proof and plasma-resistant materials like e.g. most of the plastics, metals, glasses, ceramics, caoutchouc/rubber, even foam materials.

Which materials are not really suitable for low-pressure plasma cleaning?

All materials causing a significant disturbance of the vacuum and/or plasma because of emission. This applies to some silicones and fabrics.

Plasma processes are hardly suitable for inorganic contaminations. However, workpieces with both inorganic and organic contaminations can be cleaned in combination with wet-chemical pre-cleaning.



High-precision surface etching

Flexible application-optimized process

Virtually all sorts of organic material can be plasma etched. The etching effect is based on the same chemical reactions as the cleaning effect. Only the parameters such as time and intensity must be adjusted to the requirements.

In addition to oxygen, other gases can be used which increase the etching rate significantly. In most cases, fluorinated gases as CF_4 are employed. The fluorinated radicals created in these processes are much more reactive than oxygen plasma. However, their reaction products must be retained by suitable filters.

Areas of application

- Semiconductor industry
- Circuit board industry
- Microelectronics
- MEMs

Advantages of plasma etching

- High crack penetration, therefore also suitable for micro holes
- Virtually all dielectrics etchable
- No toxic chemicals necessary
- Simultaneous treatment of all holes
- Low operating costs

Ecological and economical benefits

Compared with conventional wet-chemical methods, plasma treatment uses very little chemicals and the mainly used process gases (e.g. oxygen, nitrogen or CF_4) are harmless, easily available and inexpensive.

Therefore there are no significant expenses for occupational safety or waste disposal. Energy consumption is relatively low and there is no need of a drying process of the components because it is a dry-chemical process.

Desmearing / Back-etching

One application in plasma technology is desmearing or back-etching of mechanically drilled circuit boards. This process can be applied simultaneously to both sides of the board and all holes. Due to the outstanding crack penetration of the plasma process, holes of < 0.3 mm can be back-etched, even materials such as Teflon.

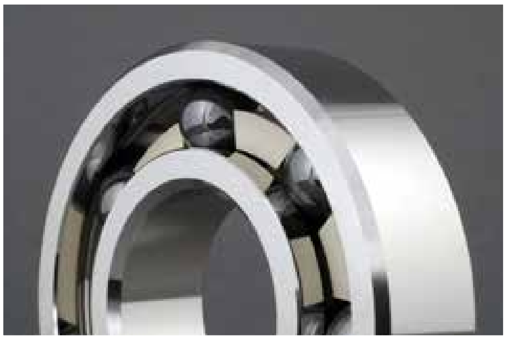
Modern circuit boards and many other electronic components base on high-grade films. Processing can take place by both plasma etching and plasma activation.

Functional coating of surfaces

A variety of coating options for many different materials

Low-pressure plasma technology is a process by which special functional groups can be deposited on surfaces. In this way, a defined coating effect can be achieved on many different materials.

Such plasma polymerization – so-called PECVD – is a relatively new coating technique and, because of the low thermal impact on the substrate, especially suitable for coating of plastics. However, it can also be used on an abundance of other materials such as metals, glass, ceramics, semiconductors and textiles.



The runout performance of hybrid roller bearings (steel ring with ceramic rollers) can be improved by plasma coating. *Photo: Cerobear GmbH*

Areas of application

- Automotive and automotive component industry
- Medical technology
- Sealing systems
- R&D
- Packaging industry

The wide variety of coating properties obtainable due to the many variable process parameters is particularly relevant for industrial coating processes.

For instance, plasma coats can use a primer for downstream processes. At the same time, such primer coats also can be used as corrosion protection.

Coating options

- Hydrophobic coats
- Hydrophilic coats
- Diffusion-proof coats
- Biocompatible coats
- Primer coats
- Anti-icing coats

Resistant – even with extremely thin coats

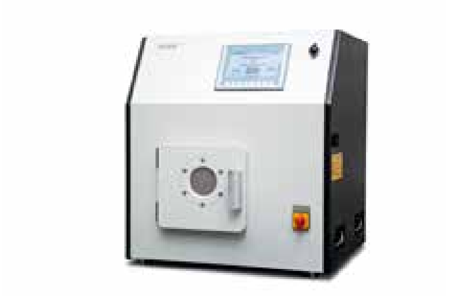
In general, plasma polymerized coats are highly cross-linked three dimensionally. Therefore, they are thermally and chemically very stable.

Advantages of plasma coating

- Wide variety of options regarding coat properties
- Low thermal stress, therefore also suitable for temperature-sensitive plastics
- High thermal and chemical stability of the coats

»The definition PECVD (Plasma Enhanced Chemical Vapour Deposition) stands for the plasma-induced material deposition.«

Standard systems for activation, cleaning, coating, etching



PINK stands for high-quality systems. The product range of standard systems reaches from the compact low-pressure tabletop device V6-G, suitable for both plasma applications in batch production and R&D test series to stand-alone systems that can be equipped with different plasma producing frequencies and capacities. Therefore, they are usable for different plasma processes.

System features

- USB port
- Ethernet interface
- Remote maintenance (VPN)
- Swing door
- Microwave source 2.45 GHz

	V6-G
Type of system	Tabletop unit
Dimensions of the chamber (W x D x H)	170 x 200 x 170 mm
Microwave power	50–300 W
Gas inlets with mass-flow-control	1
Power supply	230 V, 50/60 Hz
Power input (without pump)	0.5 kVA
Dimensions of the system (W x D x H)	640 x 710 x 710 mm

Options:

Additional gas inlets	2
Additional excitation frequencies (40 kHz, 13.56 MHz)	—
Soft start/slow vent	✓
Lateral microwave coupling	✓
Rotary table	—
Rotary drum	✓
Pullout door	—
Automatic door opening	—

			
V10-G	**V15-G**	**V55-G**	**V80-G-side**
Tabletop unit	19" cabinet	19" cabinet	19" cabinet
Dia. 215 x D 260 mm	250 x 250 x 250 mm	400 x 460 x 340 mm	400 x 500 x 430 mm
50 – 600 W	100 – 600 W	100 – 1,200 W	100 – 1,200 W
1	1	2	2
230 V, 50/60 Hz	230/400 V, 50/60 Hz	230/400 V, 50/60 Hz	230/400 V, 50/60 Hz
1.5 kVA	1.5 kVA	2.2 kVA	2.2 kVA
720 x 820 x 820 mm	670 x 900 x 1,850 mm	670 x 900 x 1,850 mm	850 x 900 x 1,850 mm

2	3	2	2
—	✓	✓	—
✓	✓	✓	✓
—	✓	—	✓
—	✓	✓	✓
—	✓	✓	✓
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Customized automation solutions for series production

Inline plasma treatment

In order to exploit the advantages of plasma technology in industrial series production, PINK offers customized solutions enabling its systems to be integrated into existing or new production lines.

The technical features are individually configured to match customer requirements, enabling the plasma process to be applied fully automatically and with maximum productivity.

V200-2G-Auto

Partially automated system for plasma cleaning. Manual loading and unloading is easier due to tables. This system can be integrated into an automated production line with minor modifications.

A suitable solution for each customer requirement

In addition to standard plants, PINK also offers customized special systems. For instance, the systems are individually designed with regard to chamber volume, excitation frequencies and controls.

In principle, the service includes comprehensive consulting, analysis of the task and development of the ideal plasma process according to customer requirements. Therefore, highest possible productivity and reliability can be achieved even for demanding purposes.

Example for a customized system.

Reel-to-reel systems for plasma treatment of flexible tapes

The reel-to-reel technology is a method especially developed for the plasma treatment of flexible tapes. The tape is continuously rewound from one reel to the other during treatment. Transportation speed depends on the type of plasma process.

Plasma processes used for tape-shaped substrates are e.g. etching, activation, coating and cleaning. Plastic films as well as metal strips like leadframes can be processed. The processing of reel with interleaf (protective foil) is also possible.

The reel-to-reel system V200-8G-K-RR cleans the surface of leadframes.

Detail of a system for the treatment of foils.

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