UPORABA PLAZME V ELEKTRONIKI
APPLICATION OF PLASMA IN ELECTRONICS

PLASMA PROCESSES

PART III: SURFACE ACTIVATION AND ASHING

I. Šorli*, W. Petasch, B. Kegel, H. Schmid, G. Liebel, W. Ries
*MIKROIKS d.o.o., Ljubljana, Slovenia
Technics Plasma GmbH, Kirchheim, Germany

Applications of plasma processes are becoming increasingly popular in many industrial and research communities. Electronics, microelectronics, automotive, aircraft, and food industry are among the most frequent plasma users. This is not surprising if we consider e.g. the field of cleaning applications. There, plasma cleaning or plasma combined with some suitable wet precleaning technique can totally replace CFC and some other toxic cleaning agents.

The first article described basic plasma physics and plasma generation, the second application of plasma in electronics, while the third one gives an overview of plasma application in the field of surface activation and ashing for trace analysis.

Technics Plasma GmbH in Kirchheim, Germany is among the pioneers and leaders in plasma technology and its application in academic and industrial environments. At the end of this article we will give an overview of their most popular plasma systems.

1.0 INTRODUCTION

Plasma is obtained by producing a discharge in gases or gas mixtures under vacuum through the application of high frequency alternating voltage. The gas in the chamber is brought to an excited (ionized) state. As well, active radicals and UV radiation are released. Electrons and UV light, resulting from the recombination processes are essential for maintaining the plasma. These components are the actual energy carriers, which are ultimately responsible for the production of chemically active radicals. This highly active process gas is capable of reacting with the surface of the material to be treated even at low temperatures. During the process fresh gas is continuously fed into the chamber. The reaction products are evacuated by the vacuum pump.

Plasma excitation via microwaves (2.45 GHz) has proved especially effective, since the efficiency of the gas discharge increases considerably with increasing frequency but still requiring very low electrical power. This results in strong, intensive ionization and production of radicals and thus a more cost effective process. Today's microwave excitation technology makes it possible to use the low pressure plasma processes economically in industrial mass production in either continuous or batch systems using large process chambers. Small bulk parts, as well as large components can be effectively cleaned and activated.

Very important issue of low pressure plasma is its penetrability. The gas enters the smallest crevices, making it possible to process three - dimensional parts with complex geometries. Another very important fact is that plasma processes are environmentally friendly and as such are alternatives to CFC cleaning processes. Thus, main advantages of low-pressure plasma technology are:

- dry process
- energy saving through low power consumption
- inexpensive supplies, cost - effective gases
- switch - off chemistry: the process stops immediately when the power is turned off, no disposal of waste
- cleaner, safer workplace, simple operation
- high penetration power into narrow spaces - an advantage in degreasing or activating parts with complex shapes
- constant process conditions, good reproducibility
- meets or exceeds air emission standards
- parts are absolutely dry after treatment

2.0 SURFACE ACTIVATION

In order to increase adhesion properties of nonpolar plastic surfaces, the treatment in a low pressure, microwave generated oxygen plasma is the key to further processing. Surface energies are raised to levels which ensure excellent adhesion before lacquering, glueing, printing, painting, foaming, coating and laminating.

In table 1 we show surface tension of most commonly used plastic materials. If for example, the paint used for painting the surface of the polymer has higher surface tension than the polymer itself, insufficient adhesion occurs.

The toughest adhesion test to the polymer surface is done with the measurement of wettability, i.e., contact angle between water drop (water has surface tension of 72 mN/m) and the treated surface, figure 1.

Three phenomena are responsible for changes in the surface characteristics after plasma treatment:

Removal of weak boundary layers

A residue free ashing process removes the surface layers with the lowest molecular weight (i.e., organic separation agents). At the same time, the chemical reaction of the oxygen radicals is responsible for the oxidation of the uppermost atomic layer of the polymer

Cross-linking of surface molecules

Oxygen radicals and UV radiation help break up bonds and promote the three dimensional cross-linking of molecules

Generation of polar groups

Oxidation of the polymer is responsible for the increase in polar groups which is directly related to the adhesion properties of the polymer surface.

Table 1: Surface tension of polymers

Polymer	Surface tension (mN/m)	Comment
Paraffin	19	problematic adhesion
PTFE	18.5	
Silicon (PMDS)	24	
PP	29	
PE	31	
PMMA	33 ... 44	good adhesion
PS	33 ... 35	
PC	34 ... 37	
PVC	40	
PET	43	
PA 6,6	46	
Epoxidharz	47	

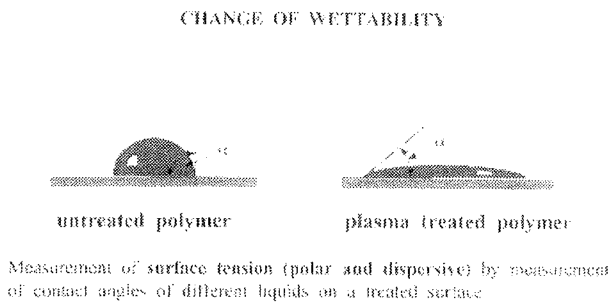


Fig. 1: Measurements of the treated surface wettability

Table 2:

result in %	UNTREATED PP	O_2 TREATED after 8 days	O_2 TREATED after 25 days
Atom C	96	81	85
Atom O	3.5	18	14.5
Bonds C-C	93	75	79
Bonds C-OH	5.5	16	14.5
Bonds C=O	1.5	6	5
Bonds COOH	/	3	1.5

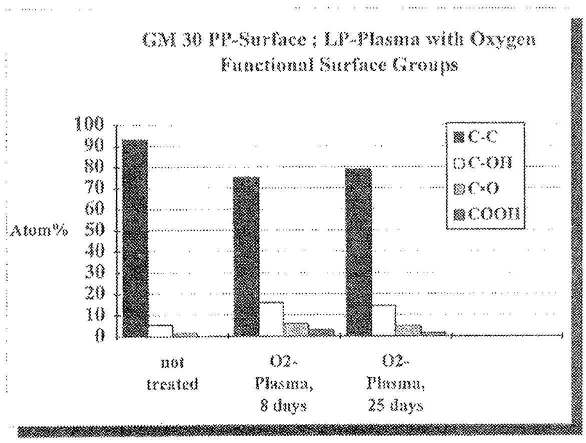


Fig. 2: Functional groups on PP surface before and after oxygen plasma treatment

As a demonstration of the above described phenomena in table 2 and figure 2 we show the results of ESCA (Electron Spectroscopy for Chemical Analysis) measurements of the untreated and treated polypropylene surfaces. The percent change in polar functional groups on the surface is obvious.

The same results are also confirmed by measurements of plasma treated polymer surface wettability. The results in table 3 demonstrate contact angles of plasma treated polymers measured with water (Treated in oxygen plasma for 2 minutes, pressure: 1.65 mbar, power: 200 W).

Table 3: Contact angles of plasma treated polymers

Polymer	Untreated, α in °	Treated, α in °
PVC (polyvinylchloride)	90	35
HDPE (High density Polyethylene)	87	22
PP (Polypropylene)	87	22
PC (Polycarbonate)	75	17
PET	71	18

Another very important and beneficial effect of plasma treatment is that the surface activation stays in effect for long period of time. However, the activated parts loose their activation if they

- are heated to high temperatures, depending on the plastic material
- are thoroughly mechanically scrubbed with a towel or paper
- become contaminated by handling

In table 4 we show the comparison of different methods used for adhesion improvement. Besides some obvious pros compared to competitive processes, plasma has one drawback. Equipment where industrial plasma processes are performed tend to be large and expensive. However, operational costs for plasma process are incredibly low (two process gases and electricity).

Industrial examples of surface activation

- Automobile rear-view mirror housings, as well as automobile bumpers are plasma treated to meet the strict requirements for paint adhesion, figure 3.
- Polypropylene car instrument consoles are activated prior to foaming with polyurethane.
- Polystyrene containers used in biomedical research are hydrophilized in low pressure plasma to facilitate wettability by liquids. These activated surfaces preserve their characteristics for several months. The material itself is not modified by plasma.
- Plastic parts of disposable syringes are pretreated prior to glueing the barrel to the cannula (needle).
- Polypropylene pen casings are plasma treated prior to printing, figure 4.

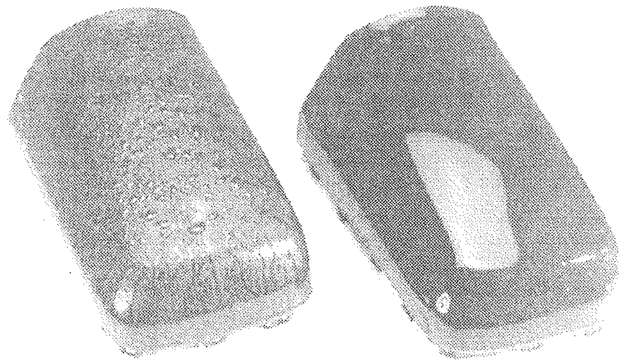


Fig. 3: Comparison of untreated and plasma treated rear - view mirror housings

Table 4: Comparison of different methods used for adhesion improvement

	FLAMING	UV TREATMENT	CORONA	NO-TREAT MATERIAL	GHz PLASMA
ACTIVATION EFFECT	1-2 days	?	6 - 7 hours	activation not needed	5 -7 days
TREATMENT OF 3D OBJECTS	difficult	limited	difficult	/	very suitable
MAX. STRESS DEVIATIONS	large 1 - 2 cm	small	up to 1 cm	none	none
SURFACE CLEANING OF PLASTICS	unsuitable	partial	unsuitable	none	very suitable
PLASMA DENSITY	low	medium	medium	/	high
ADHESION PROMOTERS	needed (contain Cl)	needed (contain Cl)	needed	none	none
OPERATIONAL COSTS	high	low	medium	expensive material	low
SAFETY HAZARD	fire risk	low chemical waste	low ozone emission	none	low enviro - friendly
INVESTMENT	low	medium	high	/	medium

- PP and PA capacitor cups and ignition coils housings are activated in plasma in a bulk process prior to mounting and filling with epoxy. This pretreatment was previously performed with chrome-sulfuric acid.
- The PC - Polycarbonate helmet visors are coated with a special lacquer: the surface must be clean and activated in plasma for this purpose.
- POM covers for ski bindings are plasma activated prior to printing
- PP loudspeaker diaphragms are plasma treated prior to glueing

Fig. 4: Treatment of polypropylene pen casings in plasma processor 3000-5D

3.0 APPLICATION OF PLASMA TECHNOLOGY IN TRACE ANALYSIS

Huge advances in the development of analytical methods, such as AAS (atomic adsorption spectro-scopy) and ICP (inductively coupled plasma) open up new frontiers of detection today, which would have been unthinkable a few years ago, As a result of this high sensitivity, the requirements for the organic matrices ashing techniques, which are decisive for the success of an analysis, have also increased considerably.

The earlier small single - or multiple - plasma chamber machines were replaced by large quartz chambers, allowing much larger amounts of substances to be processed. The improved gas flow reliably prevents the mixing of ashes when more than one sample is processed. Smooth shamber walls quarantee clean working conditions.

Plasma ashing as an alternative to wet ashing is:
- gentle
- simple
- clean
- safe
- environment - friendly

The process chamber is hermetically closed, preventing any atmospheric contamination from getting into the chamber. Only gaseous oxygen is used as an oxidant, which makes handling acids unnecessary and trace elements cannot be entrained by the acid.

Here we briefly describe some of the most typical applications:
- ashing of filters for alpha particles determination
- ashing of foodstuff for spectroscopic analysis of anorganic residues
- even materials difficult to ash by conventional methods, are easily prepared in plasma (PVC, PE, PS)
- removal of organic matrices for structural analysis
- preparation of specimen for electron microscopy

Table 5: Typical ashing times for different materials

Specimen	time needed	
Animal feed	appr. 10	hours
Blood samples	2-4	hours
Cane sugar	appr. 4	hours
Cocoa	10-12	hours
Filter	1-2	hours
Hay, grass	10-12	hours
Leaves	4-8	hours
Linseed	5-15	hours
Liver	appr.12	hours
Pumpkin seed	8	hours
Salad oil	appr. 20	hours
Wheat flour	2-3	hours
Cigarettes	appr. 1	hour
Detergent powder	appr. 15	hours
Graphite	3-4	hours
Nylon fabric	3-5	hours
Paper	1-2	hours
Polyamide fibers	2-3	hours
Polyamide granule	6-8	hours
Polyester	appr. 3	hours
Polyethylene	appr. 25	hours
PVC	appr. 20	hours
Soil samples	5-15	hours

Table 6: Overview of Technics Plasma Systems

SYSTEM	GE100	200G	300	Autoload 300 PC	440 -T2000	3000 - 5D	4000 - 7
Generator power, max W	300	400	600	1000	600	4x600	8x600
Process chamber material	Quartz	Quartz	Quartz	Quartz	Aluminum	Aluminum	Aluminum
Chamber volume, l	2	11	19.6	18	43	160	2800
Loading capacity, wafers/run	single	10 - 20	40 - 50	50	depending on substrate	/	/
System control E=single process automatic M=multistep recipe oper.	manual/ timer	E	E or M	E or M	E or M	E or M	E or M
Gas channels	2	2	2 MFC	2 MFC	2 MFC	2 MFC	2 MFC
IR temperature monitor		option	YES	YES			
Optical end point			YES	YES			
Typical applications							
Photoresist stripping	YES	YES	YES	YES+YES			
Substrate cleaning	YES	YES	YES	YES	YES	YES	
Hybrid cleaning	YES	YES	YES	YES	YES+YES		
Etching of passivation layers	YES	YES	YES	YES			
Etching of contact holes	YES	YES	YES	YES			
Polyimide etching	YES	YES	YES	YES	YES		
Depotting of electronic devices	YES+ YES						
Low temperature ashing	YES	YES+YES	YES				
Metal degreasing	YES	YES			YES+YES	YES	
Surface activation	YES	YES			YES+YES	YES+YES	
Surface activation in automotive industry						YES	YES+YES

Normally, specimen are ashed on Petri dishes or ashing plates made of Duran glass or quartz. After initial pump down cycle, oxygen is introduced at a rate of 100 ml/min, and after short stabilization time, plasma is initiated via MW 2.45 GHz magnetron source. The plasma is formed and distributed throughout the chamber, so that the entire volume can be used for specimen treatment. Typical working pressure is about 1 mbar. Reaction products are volatile and are pumped away by means of a vacuum pump.

The ashing time of a sample depends on the type of substance, its weight, ash contents, and the surface exposed to oxygen attack.
Up to 60 g specimens can be loaded in plasma processor 200 G (specially designed for ashing applications). Some typical ashing times on Petri dishes with 0.5 g - 2.0 g sample weight are given in table 5.

4.0 TECHNICS PLASMA LINE OF PLASMA SYSTEMS

With over 15 years of manufacturing experience, Technics Plasma produces plasma systems which guarantee high performance in numerous industrial and R&D applications and communities.

In the last part of the article we present in tabular form the most popular and mostly used plasma systems made by Technics Plasma. As well, their photographs are added.

5.0 LITERATURE

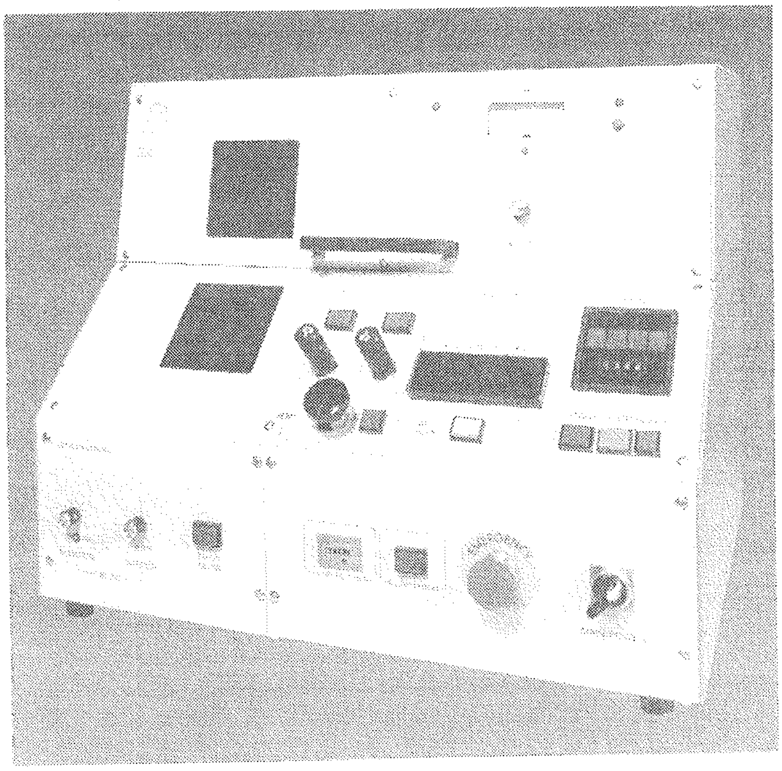
Technics Plasma GmbH, Application Reports

Nowadays, plasma systems are widely used in microelectronics and micromachining technology for resist stripping, thin film etching and bulk silicon etching. Technics Plasma also offers plasma systems specially designed to perform such tasks. However, we did not describe in detail these applications since they will be covered in several articles to be published in near future.

COMMENT: For more information about Technics Plasma systems and their applications, please call:

MIKROIKS d.o.o., Mr. Iztok Šorli
Dunajska 5,1000 Ljubljana, Slovenia
tel. +386 (0)61 312 898,
fax.+386 (0)61 319 170

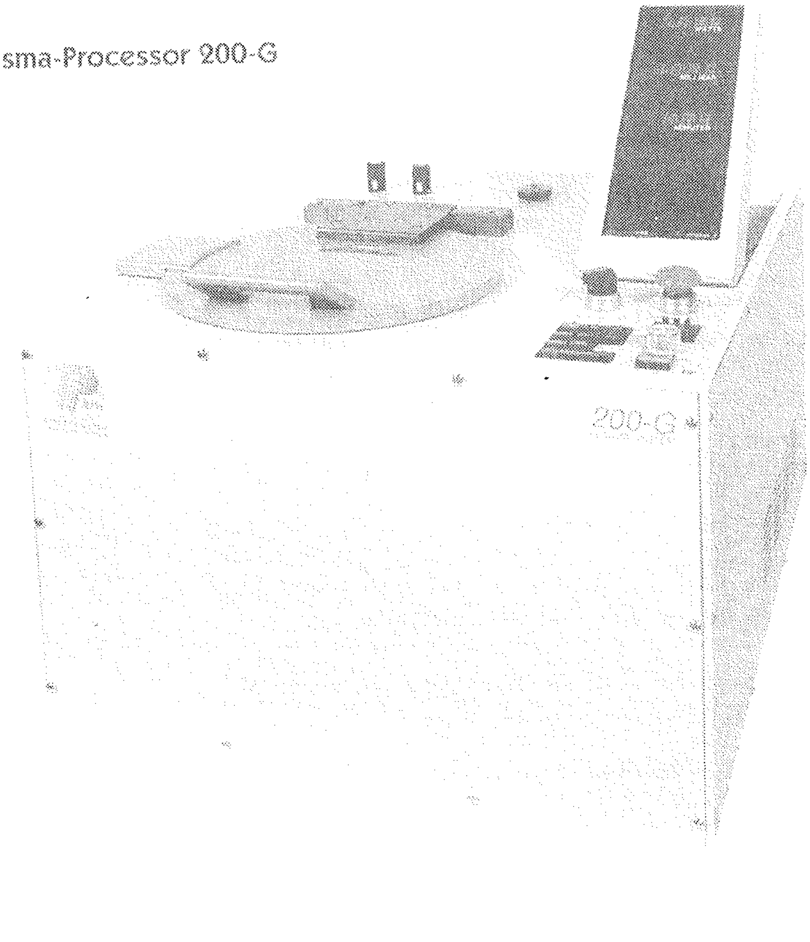
Plasmasystem GIGA–ETCH 100



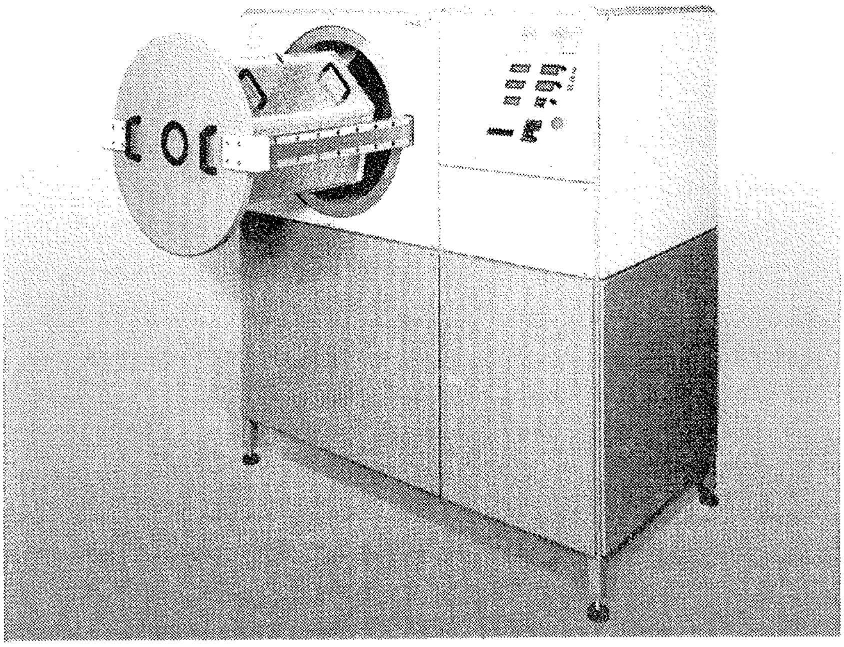
Compact low–pressure plasma system for the loboratory for

- Photoresist Stripping
- Depotting of devices
- Etching of Si_3N_4, Poly–Si and polyimide
- Low temperature ashing

Plasma-Processor 200-G

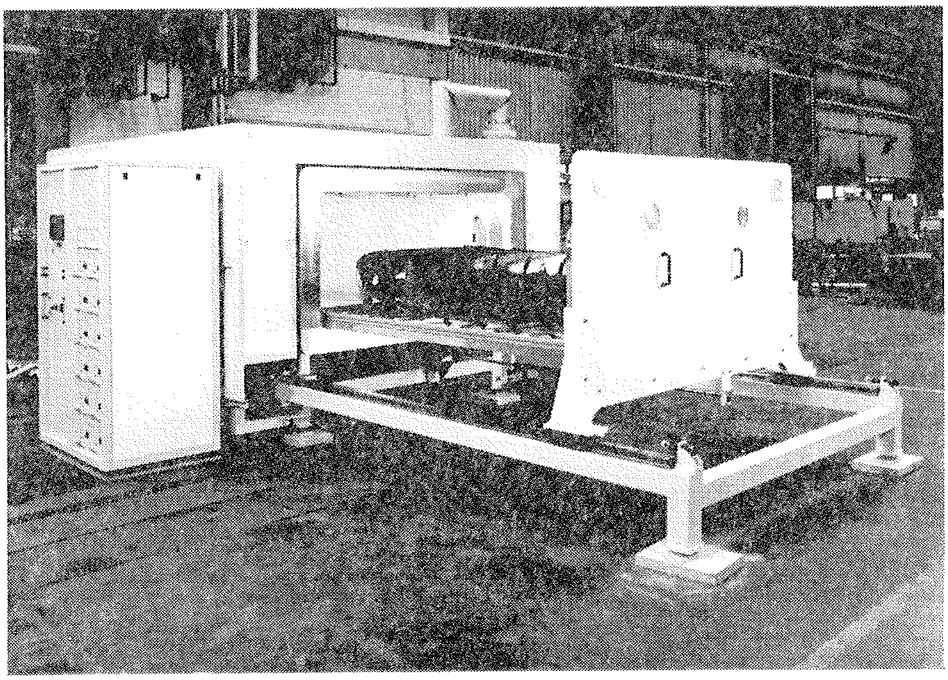


Sample carrier (Pyrex)



Mod. 3000-5 D Plasma System with bulk treatment drum

PLASMA SYSTEM 4000-7
for surface activation of plastics using microwave excitation



Industrial applications:	*Environmental advantages*
The plasma system 4000-7 is designed for treating plastic parts such as spoilers, instrument panels, wheel covers Surfaces are modified by a low pressure plasma, improving the adhesion of foam padding or paint.	In contrast to conventional treatment methods, plasma technology is environmentally clean. Only small quantities of the process gas such as oxygen are required. Additional safety precautions are not necessary