Plasma treatment has been an essential production tool for more than 30 years in the fabrication of microelectronic devices for example. Over this period, plasma processes have also permeated a much broader range of industries: automotive, medical, textiles, and plastics to name but a few. This is an overview of the technology behind Plasma.
Introduction

Today plasmas are routinely used to clean and surface treat plastic automotive bumpers, performance textiles and filter media, stainless steel syringe needles, angioplasty balloon catheters, plastic lenses, golf balls, and many other diverse products. In fact, it would be difficult to identify a modern product that has not benefitted from plasma processing at some stage during its fabrication.

Plasmas have a number of unique properties that have lead to such widespread application:

- Ability to treat complex 3D objects and micro-channels
- Environmentally friendly, no waste chemicals
- Can be almost infinitely ‘tuned’ to deliver surface specific properties
- Ability to treat temperature sensitive materials
- Treat conductors, semi-conductors and insulators alike
- Very low unit cost per treatment
- Ability to produce high value-added property to product

and many, many more
What is Plasma?

States of matter

Solid, liquid and gas are the three states of matter we are all familiar with. We can move between the states by adding or removing energy (e.g. heating/cooling). If we continue to add enough energy, gas molecules will become ionised (lose one or more electrons) and so carry a net positive charge. If enough molecules are ionised to effect the overall electrical characteristics of the gas the result is called a plasma. Plasmas are therefore, quite rightly, often referred to as the fourth state of matter.

A plasma contains positive ions, electrons, neutral gas atoms or molecules, UV light and also excited gas atoms and molecules, which can carry a large amount of internal energy (plasmas glow because light is emitted as these excited neutral particles relax to a lower energy state). All of these species can and do interact with any surface placed in contact with the plasma. By choosing the gas mixture, power, pressure etc. we can quite precisely tune, or specify, the effects of the plasma upon the surface.

Plasma treatments are performed in an evacuated enclosure, or chamber. The air is pumped out and a gas is allowed to flow in at low pressure before energy in the form of electrical power is applied. It’s important to note that these types of plasmas are actually at low temperature, meaning that heat sensitive materials can be processed quite readily.

Common everyday plasmas include:
- Fluorescent lights and energy saving light bulbs
- ‘Neon’ signs, and
- Plasma televisions of course
Plasma treatment effects

Plasmas are a ‘soup’ of energetic, highly reactive species that are able to interact with any surface which they contact. By choosing the right configuration and processing parameters we can produce specific effects upon the surface. These effects can be categorised as Plasma Cleaning, Plasma Surface Activation, Plasma Deposition and Plasma Etching and are detailed further in the remaining sections of this article.

Plasma cleaning

Plasma cleaning is a proven, effective, economical and environmentally safe method for critical surface preparation.

Plasma cleaning with oxygen plasma eliminates natural and technical oils & grease at the nano-scale and reduces contamination up to 6 fold when compared with traditional wet cleaning methods, including solvent cleaning residues themselves. Plasma cleaning produces a pristine surface, ready for bonding or further processing, without any harmful waste material.

How plasma cleaning works

Ultra-violet light generated in the plasma is very effective in the breaking most organic bonds of surface contaminants. This helps to break apart oils and grease. A second cleaning action is carried out by the energetic oxygen species created in the plasma. These species react with organic contaminants to form mainly water and carbon dioxide which are continuously removed (pumped away) from the chamber during processing.

If the part to be plasma cleaned consists of easily oxidised materials such as silver or copper, inert gases such as argon or helium are used instead. The plasma activated atoms and ions behave like a molecular sandblast and can break down organic contaminants. These contaminants are again vapourised and evacuated from the chamber during processing.
Comparison of plasma cleaning & wet chemical cleaning

<table>
<thead>
<tr>
<th>Plasma Cleaning</th>
<th>Wet Chemical (solvent/aqueous) Cleaning</th>
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<tbody>
<tr>
<td>Processes are precisely controllable through power, pressure, gas type, processing time etc.</td>
<td>Processes are very sensitive to processing time and chemical concentrations</td>
</tr>
<tr>
<td>No organic residues remain</td>
<td>Reliability depends on satisfactory neutralisation of residues which may require further processing steps</td>
</tr>
<tr>
<td>“Waste” is harmless and always in gaseous form that can be liberated directly to atmosphere</td>
<td>High volume of liquid waste which requires expensive treatment and is subject to tight regulations</td>
</tr>
<tr>
<td>Most of the gases used have no toxicity</td>
<td>Most of the solvents and acids used are extremely hazardous</td>
</tr>
</tbody>
</table>

Plasma cleaning is suitable for:

- Hyper-fine cleaning of metal surfaces
- Surface preparation of plastics & elastomers
- Surface preparation and cleaning of opthalmic and general glass products
- Ceramics
- Removing oxidation from surfaces
Plasma surface activation

Plastics, i.e. polypropylene or PTFE (polytetrafluoroethylene) are homopolar and do not bond easily. Plasmas afford an effective surface activation pre-treatment prior to printing, lacquering or gluing. Glass and ceramics can be plasma activated similarly.

Technical oxygen is usually used as the process gas, however, many plasma activations can also be carried out with just ambient air. Parts remain active for a few minutes up to several months, depending on the particular material that has been plasma treated. Polypropylene for example can still be reprocessed several weeks after treatment.

Tests of plasma surface activation

The effects upon a surface of plasma surface activation are readily seen during subsequent product processing steps but there are a number of formal test methods that demonstrate the results too:

Contact angle measurements

Water beads on an untreated surface but spreads out (have lower contact angle) on a plasma activated surface.

Dyne test inks

A pen is applied to the surface under study and a simple visual observation of wettability is made. Using pens of increasing surface tension provides a rapid identification of the approximate level of the surface energy of the sample.

Below a half treated piece of ptfe displaying better wettability characteristics in the top half where the plasma treatment was applied.

- Lower half surface energy less than 56mN/m
- Top half surface energy greater then 56mN/m

Grid cut test

Grid test cut methods [DIN EN ISO 2409] clearly demonstrate the enhanced bonding (bottom image) to plasma activated surfaces.

Before plasma treatment

After plasma treatment
How plasma surface activation works

UV radiation and active oxygen species from the plasma break up separating agents, silicones and oils from the surface. These are pumped away by the vacuum system. Active oxygen species (radicals) from the plasma bind to active surface sites all over the material, creating a surface that is highly ‘active’ to bonding agents.

**Plasma surface activation is suitable for**

- General plastics and rubber
- Medical plastics
- Consumer electronics plastics
- Automotive components
- Aerospace components

LOW SURFACE ENERGY
Difficult to Bond

Plasma Surface Activation

BEFORE PLASMA TREATMENT

Oxygen

Plasma Surface Activation

DURING PLASMA TREATMENT

Oxygen Activated, Easy to Treat Surface

Plasma Surface Activation

AFTER PLASMA TREATMENT
Plasma coatings

In plasma coating a nano-scale polymer layer is formed over the entire surface area of an object placed in the plasma.

The coating process takes just a few minutes. The coating produced is typically less than 1/100th thickness of a human hair, colourless, odourless and doesn’t effect the look or feel of the material in any way. It is a permanent coating too, being bound to the material surface on an atomic scale.

Plasma coatings are one of the most exciting areas of plasma technology, offering enormous potential to enhance a material’s function and value over a wide range of applications. They deliver two main categories of surface property; totally liquid (water & oil) repellent, or totally wettable.

**Hydrophobic plasma coatings**

Specific treatments render surfaces totally repellent to water, solvents and oils.

**Hydrophilic plasma coatings**

Hydrophilic plasma treatments render surfaces permanently wettable.
How plasma coatings work

Monomers are introduced with the plasma feed gas. Monomers are small molecules which will, under the correct conditions, bond together to form polymers. Plasmas create the right conditions at the surface of the material for this to happen both quickly and efficiently. Different monomers are used to produce hydrophobic and hydrophilic surfaces.

**Plasma coating is suitable for:**
- General plastics and rubber
- Performance textiles
- Consumer electronics plastics
- Automotive components
- Aerospace components
- Filtration media
- Metals, glass, ceramics and composites
- Medical plastics
Plasma etching

Plasma etching is used to ‘roughen’ a surface, on the microscopic scale. The surface of the component is etched with a reactive process gas.

Material is precisely sputtered off, converted to the gas phase and sucked away via the vacuum system. The surface area is greatly increased, making the material easily wettable. Etching is used before printing, gluing and painting and is particularly useful for processing of e.g. POM and PTFE, which cannot otherwise be printed on or bonded.

Reactive ion etching

Reactive ion etching delivers a highly directional flux of energetic, reactive ions to the material surface. In doing so, a precisely controlled patterning of the substrate occurs as un-masked sample is etched away by the reactive ions. Each of our plasma systems can optionally be fitted with a reactive ion etch electrode making them a perfect, low cost laboratory development tool in applications such as semiconductor or organic electronics research.

Plasma etching effects

<table>
<thead>
<tr>
<th>Untreated surface</th>
<th>Treated surface</th>
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<tbody>
<tr>
<td><img src="image.png" alt="Untreated surface" /></td>
<td><img src="image.png" alt="Treated surface" /></td>
</tr>
</tbody>
</table>

Plasma etching is suitable for:

- POM, PTFE, FEP, PFA
- PTFE compounds
- Structuring silicon
- Photoresist ashing
Activation | Cleaning | Coating | Etching