Plasma Surface Modification for Cleaning and Adhesion

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When manufacturers scramble to find processes of surface cleaning and modification that ensure successful products, they are presented with a variety of choices. Recent advances in the use of polymers and the resulting need for hydrophilic surfaces for adequate adhesion has fueled the development of the plasma surface modification industry. Also as component and circuit size continues to shrink, plasma gas treatment is fast becoming the choice of method for cleaning electronic components and BGA' s.

Plasma treatment for surface modification is used to produce hydrophobic or hydrophilic surfaces on metals, plastics, glass or polymers. Teflon and metal surface modification for enhanced adhesion are examples of applications described

When plasma gas interacts with the surface of polymers four primary effects can occur: the removal of organic materials, CASING or cross-linking via activated species of inert gases, ablation, and surface chemical restructuring. Discussion and graphics will be presented to demonstrate, through contact angle measurement, organic materials removal and surface restructuring. Surface chemical restructuring, by adding polar functional groups to the surface structure, greatly increases the surface energy and associated adhesion to other materials. Ablation roughens the surface increasing the total contact area between the adhesive and the subsurface.

Plasma treatment is used to clean away the unwanted materials at the molecular level to a greater degree than can be achieve with wet chemical processes. Drill smear on electronic circuit boards, photo-mask de-scumming and parylene removal are among other applications described.

Outline

I. Introduction and description of plasma
II. Sources of plasma
III. Four effects - organic removal, CASING, ablation and surface chemical restructuring
IV. Plasma induced reactions
V. Plasma equipment and processes
VII. Case studies

As manufacturers scramble to find surface cleaning and modification processes that will ensure profitable product success rates, they are presented with a variety of choices. Plasma is fast becoming the first among the choices available. Recent advances in the uses of polymers and the resulting need for hydrophilic surfaces for adhesion have fueled the development of the plasma surface modification industry.

Plasma is an environmentally safe method of organic removal and surface modification. Plasma processes can be tailored to produce hydrophobic or hydrophilic surfaces on metal, plastic, glass or polymers. Knowing how plasma addresses the adhesion is the first step for considering it in a manufacturing process. Experience has clearly demonstrated the interaction mechanisms between polymer surfaces and plasma. This experience can be leveraged for a wide range of applications.

WHAT IS PLASMA?

Plasma is loosely defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. It has been dubbed the “fourth state” of matter because of its properties that are similar to those of the gas and liquid.

Two types of plasma exist - high temperature and low temperature. High temperature plasma is found at atmospheric pressure in its manmade form as a plasma torch such as that used in stainless steel deposition, or occurring naturally as lightning. Low temperature plasmas, used in surface modification and organic cleaning, are ionized gases generated at pressures between 0.1 and 2 torr.

Low temperature plasmas work within a vacuum chamber where atmospheric gases have been evacuated typically below 0.1 torr. These low pressures allow for a relatively long free path of accelerated electrons and ions. Since the ions and neutral particles are at or near ambient temperatures and the long free path of the electrons, which are at high temperature or electron-volt levels, have relatively few collisions with molecules at this pressure the reaction remains at low temperature.

PLASMA GENERATION

The ionization of the gases is accomplished by applying an energy field using one of three source frequencies regulated by the federal government:

- Low frequency - less than 100 KHz
- Radio frequency (RF) frequency - 13.56 MHZ
- Microwave (MW) frequency - 2.45 GHz.

Frequencies selected for the energy field source are controlled by international agreements to prevent use of source frequencies, which would interfere with worldwide communication bands. Low frequency is the least expensive method of energy field generation. Unfortunately, Low frequency is also the least efficient method for cleaning action and surface modification to the manufacturers.

The efficiency of the reaction is related to the energy necessary to sustain ionization, the intensity and the frequency of vacuum ultraviolet radiation (VUV). Low frequency plasma scores low on all counts - it is the reason most plasma manufacturers use RF or MW frequency sources. AST Products uses almost exclusively RF sources because of the overall advantages associated with this method. RF plasmas exhibit significantly higher levels of VUV, which in part explains the higher concentrations of electronically charged particles than found in other plasma sources. RF plasmas have also been noted to be more homogeneous, a trait that is critical in treating irregularly shaped and overly large objects.

MW source plasmas are generated downstream or in a secondary environment. Downstream is defined as the plasma generated in one chamber and drawn by a vacuum differential into the work area or another chamber. Though this can be advantageous for organic removal from ion sensitive components it also produces a less homogeneous process resulting in the compromising of uniformity across the work area. In surface modification the effective depth of the modification is tens of nanometers so the uniformity of the process becomes increasingly important, rendering MW source plasmas a less desirable choice.

Plasma interaction with the surface of the work piece causes several resultant effects, each of which has a reaction to the adhesion process. These effects are but are not restricted to:

- Organic removal
- CASING (Cross-linking via Activated Species of Inert Gases)
- Ablation or etching
- Surface chemistry restructuring

ORGANIC REMOVAL

A major problem that prevents adequate adhesion is the presence of organic contamination on the surface. Contamination may exist in the form of residues, mold release agents, anti-oxidants, carbon residues or other organic compounds. Oxygen plasma is excellent for removing organics and is commonly used for this purpose. Oxygen plasma causes a chemical reaction with surface contaminants resulting in their volatilization and removal from the plasma chamber. Care must be taken in selection of cleaning process parameters to ensure that organics are completely removed. It is possible to “surface modify” the contamination instead of removing it and thus still have a barrier layer which will cause adhesion to fail. Critical parameters may include sufficient power density to remove but not polymerize the organics or the addition of other gases to facilitate the prevention of polymerization.

When exposed to the RF energy field, oxygen (O_2) is broken down into monatomic oxygen (O), O^+ and O^-. O at pressures above 0.1 torr is the most reactive element in the plasma and will readily combine with any organic hydrocarbon. The resultant combination is water vapor, CO and CO_2, which is carried away in the vacuum stream. The reaction is by its nature complete with no residual surface products, however non-organics such as salts are not so readily removed.

Sufficient RF energy must be applied to produce a high plasma density. Lower power densities not only remove contamination at a slower rate but also can actually impede the removal process. While the top layers of organic are being removed with low power density, underlying layers may cross-link in three dimensions creating a stable but un-removed new structure:

$$\mathbf{-CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-----------}>\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\ \text{----------------}>\ \text{-}\ CH_2\text{-}CH_2}$$

The potential for the above situation to occur demonstrates the need to carefully monitor power density. Whether or not organic removal is complete can be assessed through the use of contact angle measurement. Actual surface energy can be calculated, using the same method and the application of three different liquids. Contact angle analysis for organic removal (Figure 1) and for effects presented later in this article is done by AST Products, Inc. VCA-2500 system using certified water.

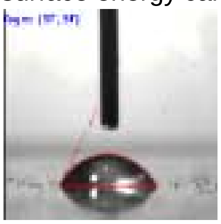
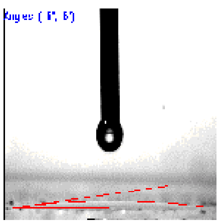


Figure 1
Aluminum coupon with cutting oil contamination

Contact angle before plasma cleaning (using certified water): 57/54^o



Contact angle after plasma cleaning: below readable limits of <3 deg

CASING

CASING is an acronym referring to the use of inert gas as the plasma for treatment on polymer surfaces. When generating plasma using inert noble gases such as helium or argon, the plasma would break C-C or C-H bonds by ion and VUV bombardment. These free radicals in turn recombine on the surface causing a stable cross-linking of the surface structure. The improved bond strength of the surface can be a very desirable effect.

As in other plasma reactions, CASING formation is at or just below the polymer surface with the radicals formed having a long life. This can give rise to post-plasma reactions but may also be used to the advantages. In the case of PTFE (Teflon) treatment, AST Products has found that pretreatment with helium followed by the plasma of ammonia (NH_3) will facilitate the bonding of a barrier layer to the PTFE, which in turn will be receptive to adhesion. This is illustrated with contact angle measurements made before and after treatment (Figure 2).

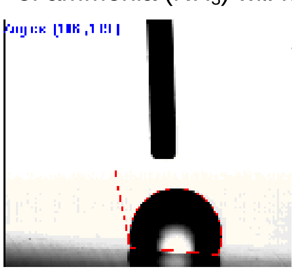
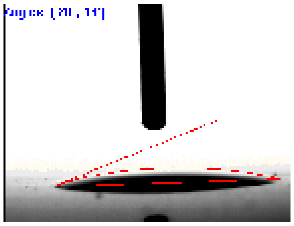


Figure 2
Adhesion improvement to PTFE surface

Before plasma treatment: contact angle of 106/107^o using certified water



After He/NH_3 plasma treatment: contact angle of 20/18^o.

ABLATION
Etching of surfaces also can also be accomplished by plasma. Roughening of the surface can play a significant part in adhesion by increasing the total contact area between the adhesive and the subsurface. Etching is a result of gas selection or the length of time the surface is exposed to the plasma. Ablation can be accomplished with either active or inert gases and can be run to excess causing extremely porous surfaces by too long of an exposure to the plasma.

The semiconductor manufacturing industry has used plasma etching as a primary treatment method for over 20 years. In addition the circuit board industry has used plasma as a means of etching polymers smeared in the drilling process. Hole smears prevent contact with plated through holes on multi-layer circuit boards. Smears are easily removed by plasma ablation regardless of how small the holes are.

SURFACE CHEMICAL RESTRUCTURING
Perhaps the plasma treatment effect offering the greatest potential is modification of the surface structure. We briefly discussed it in the application of a barrier layer during the treatment of PTFE. By adding polar functional groups to the surface structure of the polymer we can greatly increase the surface energy and thus aid the adhesion to other substrate materials.

Plasma treatment can be used to provide for the oxidation of the surface in much more uniform methods than by corona discharge or flame treatment. Large irregular surfaces also can be treated with little possibility of over-treatment, a drawback of both flame and corona methods. Plasma has shown great gains as an effective method in the treatment of automotive polymers such as car bumpers and panel boards. Elimination of primer coatings for paint adhesion by plasma surface preparation is currently the method of choice by several automobile manufacturers.

In addition to rendering surfaces hydrophilic for adhesion, plasma can also render a surface hydrophobic. Formation of barrier layers on chemical tanks and even textiles are possible by the application of fluorinated plasmas.

PLASMA REACTIONS
Reactions fall into two categories: chemical and mechanical. Chemical reactions result from a chemical interaction of the plasma with the surface of the product or contaminants attached to the surface. These reactions include oxidation and ablating the surface with such gases as oxygen, fluorine or chlorine.

Mechanical reactions are generated with the use of noble gases such as argon or helium. Since these inert gases exist in their monatomic state the reaction is a kinetic energy transfer or, in simple terms a molecular scale sand blast. Dislodged contaminants can be swept away in the vacuum stream before they redeposit on the product or recombine on the product surface by selecting the proper process parameters. Inert gas plasma is also used to remove organics and particulate from surfaces, which might readily oxidize such as silver or copper.

THE PHYSICAL EQUIPMENT

All current plasma systems fall into the same basic configuration:

1. A vacuum chamber for the reaction.
2. An energy source for gas ionization.
3. Control circuitry to regulate the time, gas flow and amount of energy.
4. A vacuum system to provide the low pressure environment.

THE CHAMBER

Chambers are manufactured in either metal or glass depending on the application and the method of ionization. Quartz chambers are used in highly critical environments where sub-micron particulate generation is an issue. This includes the semiconductor, hybrid and medical analysis industries.

For industrial applications, metal chambers are more prevalent and allow for the rougher handling environment accompanying that industry. Systems are even produced with tumbling chambers for surface modification of a large volume of small parts. Aluminum chambers offer an advantage over stainless steel chambers in that aluminum will develop a natural oxide layer that becomes a tough barrier to secondary reactions. Even the best stainless steel has been known to oxidize in a plasma environment and over time the oxidized surface can be a source of undesirable particulate.

USES

Plasma systems range from a small two-inch chamber to ten-foot walk-in chambers capable of processing as many as seven automobile bumpers at a time. Though there are standard sizes available the customer’s needs should dictate the system.

The growing use of plasma treatment for surface modification has given rise to continuous operation or in-line plasma systems. These systems are attempting to address the web and sheet treatment of commercial products. Batch processing is still less expensive due to the vacuum limitations of continuous operations. Following are several case studies of plasma applications.

DEGREASING

A controlled study to determine the effectiveness of the removal of common oils such as 143AA, 5606, 24139 grease and 2190 TEP was conducted by a US government agency in conjunction with AST/Plasma Science. Stainless steel coupons were cut 1" X 1" and weighed. A drop of oil weighing 10-12 mg was applied to each coupon and then exposed to different plasmas. Table 1 illustrates the removal effectiveness of different plasma gas combinations.

Table 1
Oil and Grease Removal

Contaminant	Plasma Gas	Plasma Treatment Time, minutes	Removal, percent
143AA Oil	Oxygen	15 min.	100.
5606 Oil	Oxygen	8	100
5606 Oil	Oxygen	5	100
5606 Oil	Argon	15	70
24139 Grease	O_2/CF_4	15	100
2190 TEP Oil	O_2/CF_4	15	100
5606 Oil	Room Air	15	87

PARYLENE RESIDUE REMOVAL
Connectors with residues of parylene inside the female assemblies were exposed to O_2/CF_4 plasma for 20 minutes. All traces of parylene were removed from inside the connector housings without adverse effect to the assembly. Removal of parylene was critical to the application of adhesives in further production steps.

PTFE SURFACE MODIFICATION
PTFE sheets were received with a contact angle of 106^o. After exposure to the plasma of helium followed by NH_3, the contact angle was reduced to 20^o. The lower contact angle is representative of a higher surface energy, which would allow adhesion. The surface was effectively changed from hydrophobic to hydrophilic.

AUTO BUMPER CLEANING
Automobile bumpers are being processed in an in-line plasma system immediately following mold injection. Mold release and organic are removed allowing adhesion of paint without a primer phase. Bumpers are processed seven at a time in a batch in-line assembly operation for a total cost reduction of 50 percent over previous cleaning methods.

ORGANIC REMOVAL FROM GLASS PANELS
Glass panels with organic contamination were received with contact angle measurements of $60\text{-}75^o$, less-than-one-minute plasma process produced contact angle of $1\text{-}3^o$.

DESCUMMING PHOTOMASKS
After the photoresist on chrome, photomask was developed using standard photo-chemical processes they were then treated with the oxygen plasma. Residual resist was removed with the plasma oxidizing action. Average line width was reduced approximately 50 percent, to 0.03 um, and uniformity of the surface was significantly increased.

CONCLUSIONS
Plasma processing is effective for final cleaning and surface modification for organic contaminant removal prior to adhesion. It also can be illustrated that plasma can be used to alter surface characteristics and even produce hydrophobic results.
Plasma can be applicable to any geometry, making it especially useful in modifying complex polymer surfaces. As the uses of polymers increases the need for surface preparation will increase to allow the adhesion of paints, coatings and adhesives.

Plasma modification for adhesion improvement will continue to grow as a cost-effective and environmentally friendly alternative to chemical processes. Plasma is especially effective in the surface modification of small and irregular shaped polymers regardless of the minuteness of critical dimensions.

References

1. Wetterman, Bob. “Contact Angles Measure Component Cleanliness,” Precision Clean, October, 1997, pp 21-24.