Atmospheric Plasma – A New Surface Treatment Technology for Cleaning PCBs

Rory A. Wolf
Enercon Industries Corporation
Menomonee Falls, WI

Abstract

Low-pressure plasmas have been used for many years to surface clean and functionalize substrates prior to downstream converting operations; therefore, the benefits of plasma treatment are well recognized: reduced degradation of surface morphology, higher treatment (dyne) levels, elimination of backside treatment, and extended life of treatment over time. However, the complexity, slow speed and high cost of these contained vacuum plasma systems made them impractical for all but the most esoteric applications. Now a system has been developed that allows plasmas to be sustained at atmospheric pressure in a way that permits the surface cleaning of PCB substrates on a continuous web handling system similar to a corona treating system. The atmospheric plasma process allows treatment using a broad range of reactive gases and has been successfully tested on various metals, films, papers, foams, and powders. Further, depending upon the cleaning requirement and type of material, roll-to-roll processing speeds in excess of current PCB vacuum processing speeds can be achieved. The particular solution of significant importance to the circuit board fabrication industry described in this paper and provided by atmospheric plasma systems is removing the residues of contaminants from sensitive surfaces without damaging them to increase yields. The application of atmospheric plasma technology to PCB manufacturing and its critical parameters will be presented because of its potential increase in processing speed in sheet and roll-to-roll orientations.

Introduction

The relentless drive to higher performance and greater miniaturization, coupled with the need to incorporate more functionality in electronic goods is putting continuous pressure on electronics designers and manufacturers to increase the packaging and interconnect densities of their electronics assemblies. This has resulted in semiconductor components having greater numbers of interconnects and smaller packaging profiles. In order to accommodate these packages, and higher density interconnects, all the features on a PCB, such as track widths and hole diameters are all having to become smaller as well. As evidence of this, PCBs with layer counts from one layer to 50+ layers are being produced. Circuit board sizes range from less than the size a fingernail to as large as a dinner table. Copper foil can reach thickness as thin as 1000 angstroms. Circuit features in some applications are discernable only with a microscope with metal traces ranging down to less than 10micron. Consequently, the performance demands on PCB laminates are also increasing significantly and there is a move to introduce new laminate materials that can meet these challenges.

As a result of this trend, traditional manufacturing methods for pre-treating new generation components of these layered boards and removing residue are no longer as cost-effective. More specifically, process flows which employs low-pressure (vacuum) plasma chambers has traditionally been labor-intensive in its use to provide surface treatment and cleaning of PCBs of historical configurations. When considering plasma treatment in vacuum, the low pressure levels in vacuum coating chambers allow the generation of uniform plasma, usable for effective treatment of many surfaces. As such, the technology is also widely used for web coating application and for the treatment of 3D objects like automotive bumpers. Although the uniformity of the plasma allows for high treatment levels, these applications require cycle times which may not meet new equations for worldwide competitiveness.

Innovations in PCB material technology, such as those which offer higher thermal resistance, and the use of smaller geometries as portrayed above, have led to an increased requirement for plasma processing at higher speeds and at multiple steps in the manufacturing cycle. Multilayer PCBs with high-density interconnects require designs with finer pitch, and the use of new material technologies with high yield potential. Laminates which include those based on cyanate esters, allylated polyphenylene ethers, and the so-called BT-epoxy and tetrafunctional epoxy systems may resolve coefficient of thermal expansion and speed issues, but new impasses to productivity can arise during the board manufacturing process where the use of traditional processes is limited. As another example, it is known that chemical processing with high pH permanganate solutions is limited due to the inability of the fluid to fully penetrate the small vias found in multilayer PCBs. It is also known the wet chemistry approaches which involve acid etching have difficulties etching polyimide dielectric materials.

Certainly, complex PCB constructions with ever-increasing layers and circuit densities benefit from plasma treatment for descum, desmear, removal of carbon-based organics, PTFE activation, and surface preparation. Plasma processing of various board types with high aspect ration holes and various via configurations using vacuum plasma technologies have been historically sufficient. However, although consumption costs are moderate with vacuum plasma systems, initial capital costs can be substantial as the need for increased processing capacities are considered.

The Atmospheric Plasma Process

A plasma is an ionized gas, a gas into which sufficient energy is provided to free electrons from atoms or molecules and to allow both species, ions and electrons, to coexist. A typical vacuum plasma system consists of four major components: the vacuum chamber, electrodes, vacuum pump and an RF power supply. Within PCB applications, the PCB panels are suspended between a pair of electrodes located within the vacuum chamber. A vacuum pumping system is utilized to maintain a plasma process pressure in the low milliTorr range. Source gases are introduced through mass flow controllers at a specified flow rate. Once the desired process pressure is achieved, radio-frequency power is applied to the electrodes to initiate the plasma process.

The high functionality of a uniform plasma discharge in vacuum has driven many efforts to establish a uniform glow discharge at atmospheric pressure, making this technology applicable to processes at atmospheric pressure and hence avoiding expensive vacuum equipment. Efforts have been reported from groups around the world. A stable glow discharge free of filamentary streamers is developed using noble gases, whose high metastable phases allow the steady glow discharge. In order to reduce the consumption of these gases to a minimum the gas is injected directly into the discharge gap (between the PCB component and the discharge electrode). Doing it this way also allows the injection of other treatment gases, which get highly ionized in the discharge and which allow to address the specific chemistry required for a particular PCB application. Depending on the gas or combination of gases, a different reaction can occur on the sample surface.

Figure 1 - A homogenous discharge between two electrodes of an atmospheric plasma system, interfacing with a treatment material.

Four major effects take place on the surface of the polymer film during a treatment with ionized gases:

- **Electron Bombardment**: Electrons, generated in the electric field of a plasma, hit the surface with a wide distribution of energy and speed. This will lead to chain scission in the upper layer of the treatment material, but can also create crosslinking, therefore in reinforcing of the material.

- **Ion Bombardment**: Ions, generated in the electric field of a plasma, hit the surface of the polymer surface with a distribution of different energy and speed. This leads to etching and sputtering, therefore cleaning of the surface substrate. Effective removal of low molecular weight structures can be performed.

- **Excitation of Gases**: Ionization of gases also means the presence of many excited species in the gas. By using the right mixture of gases, those excited species can react with the surface to create functional groups such as hydroxyl (-OH), carbonyl (-C=O) carboxyl (-COOH) or amino (NHx), which exhibit high polarity and change the base/acid interaction at the surface.

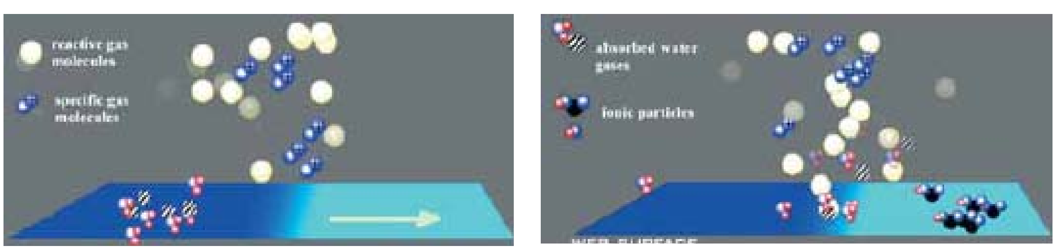

Figure 2 - Reactive gases are diffused toward the surface under the influence of external fields. Low molecular weight materials such as water, absorbed gases and polymers fragments are knocked off the surface to expose a clean, fresh surface. At the same time a percentage of the reactive components in plasma with sufficient energy bond to the freshly exposed part of the film, changing the chemistry of the surface and imparting the desired functionalities.

Atmospheric plasma glow discharges can be used as a dry etch process for the removal of drill smear and for etchback. Desmearing holes refers to the removal of a small amount of epoxy-resin from the hole barrel including any that may have been smeared across the copper interface during drilling. The smear on the copper surface, if not removed, would prevent interconnection between it and the electroless copper which is to be plated in the hole barrel. Etchback, performed less frequently on standard materials due to the advances in the performance of desmear chemistries and the subsequent relaxation of most specifications, is the removal of a significant amount of epoxy-resin and glass fibers (as much as 1 to 3 mils) that leaves the copper interface protruding into the hole. The protruding copper surface allows a large surface area for the interconnection with the subsequent copper plating and the surfaces exposed by the removal of epoxy cannot have been smeared during drilling.

Kapton® and Teflon® activation has also been accomplished by atmospheric plasma processing. For example, atmospheric plasma has increased the surface energy of Teflon® from 18 dynes/cm to levels which provide excellent lamination and wettability for plating through-holes without use of wet chemicals. In fact, all PTFE materials require plasma activation to change the surface energy for electroless copper adhesion.

Atmospheric plasmas are being employed to remove photoresist residue that can remain after developing fine pitch circuitry on panels and inner layers. Currently, photoresist is stripped from the outer layers using wet chemistries, and often in the same bath or spray chamber as the inner layers. Although resist stripping is a one-tank operation, both the developer and the stripper have short bath lives (often measured in hours), and these operations generate a large volume of waste process fluid. With the appropriate amount of dwell or exposure time, utilizing atmospheric plasma processes can significantly reduce, if not eliminate, the generation of waste stripping fluids.

Experimental Evidence

There are many construction variations with regard to printed circuit boards. For instance, the functionality of a PCB is directly related to the thickness of the copper laminated to the surfaces. The amount of current carried by the board dictates the thickness of this copper foil. Normally the thickness of the copper foil is standard. Also, you can choose between different board types for material and the number of layers. For reviewing the performance of atmospheric plasma in removing photoresist, a construction utilizing two layers of copper, one each side of the board, was integrated into an experimental protocol with the results detailed below:

Table 1 – Atmospheric Plasma Photoresist Cleaning Protocol

Interface Material	Electrode Type	Electrode Width	Processing Speed	Power Density	Reactive Gas Chemistry	Surface Contact Angle
Copper layer	Ceramic	1524mm	5 fpm	$120W/ft^2/min$	<10% Oxygen	< 16°
Copper layer	Ceramic	1524mm	5 fpm	$120W/ft^2/min$	<15% Oxygen	< 10°
Copper layer	Ceramic	1524mm	5 fpm	$120W/ft^2/min$	<20% Oxygen	< 5°

As summarized in Table 1, the non-thermal atmospheric plasma glow discharge system employed to clean the copper layer of resist created higher levels of hydrophilicity as levels of reactive oxygen were increase relative to the plasma-generating carrier gas. Contact angles below five percent were measured, indicating that low molecular weight organics were effectively removed from the copper surface as a priming step prior to lamination. It is important to note that the high density, RF-generated plasma field used to treat the copper layers was contained within a continuous design, meaning that processes such as resist removal by plasma treatment may be achieved through continuous conveyance of either sheet or web forms of PCB construction layers. Because such designs can be scaled to meet productivity objectives, increasing power density gas chemistry flow rates will directly enable increased processing speeds. This is diversely different from traditional batch (chambered) plasma cleaning systems which advocate a two stage treatment process which can take up to one hour of cycle time per batch.

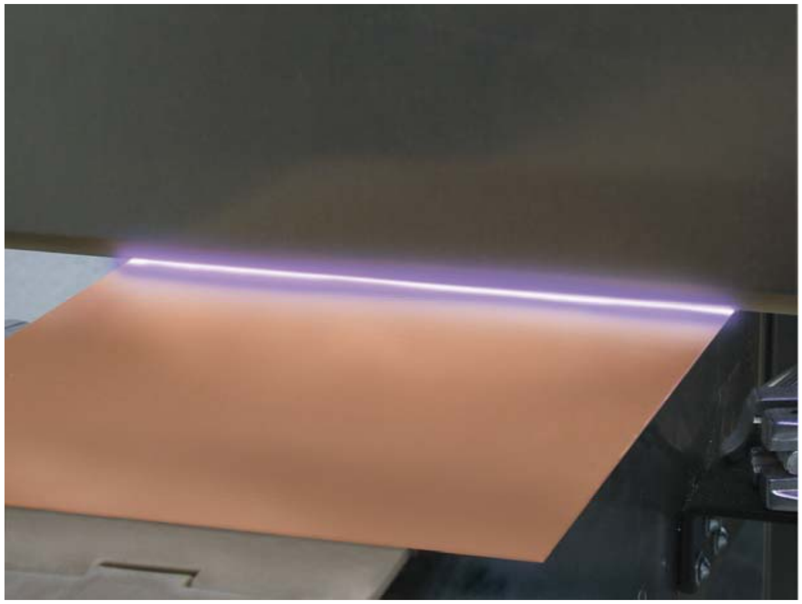

Figure 3 – Non-Thermal Atmospheric Plasma Discharge PCB Cleaning Station Removing organics from copper layer.

Summary

Printed circuit boards must be cleaned to the molecular level before electronic components can be attached to preserve the contact between the board and the component. Additionally, when preparing certain critical substrates during a coating process, it is important to achieve molecular level cleaning so that the coating properly adheres to the substrate surface. Atmospheric plasma cleaning would benefit these cleaning processes because the volatilizations caused by the ionized gas clean to the molecular level while reducing hazardous material use, waste, and air emissions. In-line, or continuous, atmospheric plasma cleaning also reduces manpower or labor time traditionally involved with cleaning by batch processes and can guarantee the quality of the clean on the first application.

REFERENCES

1. L. Fierro. J.D. Getty, “Plasma Processes for Printed Circuit Board Manufacturing, Circuitree, 2003.
2. C.M. Chan, “Polymer Surface Modification and Characterization”, Hanser/Gardner Publishers, Munich, 1994
3. R. d’Agostino, et al., “Plasma Treatment of PET for Improving Al-Adhesion”, SVC, 41st Annual Technical Conference Proceedings, 1998
4. F. Arefi-Khonsari, M. Tatoulian, J. Kurdi, J. Amouroux, “Study of Plasma Treated Polymers and the Stability of the Surface Properties”, Proceedings of the Joint International Meeting ECS and ISE, Paris, 1997
5. S. Meiners, J. Salge, E. Prinz, F. Förster: Surface modification of Polymer Materials by Transient Gas Discharges at Atmospheric Pressure. Proceedings 5th Int. Conf. on Plasma Surface Engineering, Garmisch-Partenkirchen, Germany, Sept. 1996
6. W. Decker, “Photo-CVD of SiOx Layers on Thermoplastic Films at Atmospheric Pressure”, Publisher: Papierflieger, Germany, 1998, ISBN 3- 89720-176-3
7. V. Cassio, F. Rimediotti, “Plasma Pre-Treatment in Aluminum Web Coating: A Converter Experience”, SVC, 42nd Annual Technical Conference Proceedings, 1999
8. W. Decker, A. Yializis, “Surface Functionilization of Polymer Films and Webs using Subatmospheric Plasma”, SVC, 41st Annual Technical Conference Proceedings, 1998
9. S. Okazaki, M. Kogoma, “Development of Atmospheric Pressure Flow Discharge Plasma and its Application on a Surface with Curvature”, J. Photopolymer Science and Technology, Vol. 6, No. 3, 1993, pp 339 – 342
10. L. Bardos, H. Barankova, “Radio Frequency Hollow Cathode Source for Large Area Cold Atmospheric Plasma Applications”, Proceedings of the International Conference on Metallurgical Coatings and Thin Films, 2000
11. A. Yializis, S. Pirzada, W. Decker, “Steady State Glow Discharge Plasma at Atmospheric Pressure”, US-Patent Serial # 09/241,882

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Atmospheric Plasma - A New Surface Treatment Technology for Cleaning PCBs

Presented by

Rory A. Wolf
V.P. Business Development
Enercon Industries Corporation

- Relentless drive to higher performance and greater miniaturization
- Need to incorporate more functionality in electronic goods
- Pressure on electronics designers and manufacturers to increase the packaging and interconnect densities of their electronics assemblies.
- Greater numbers of interconnects and smaller packaging profiles.
- Higher density interconnects such as track widths and hole diameters are all having to become smaller.

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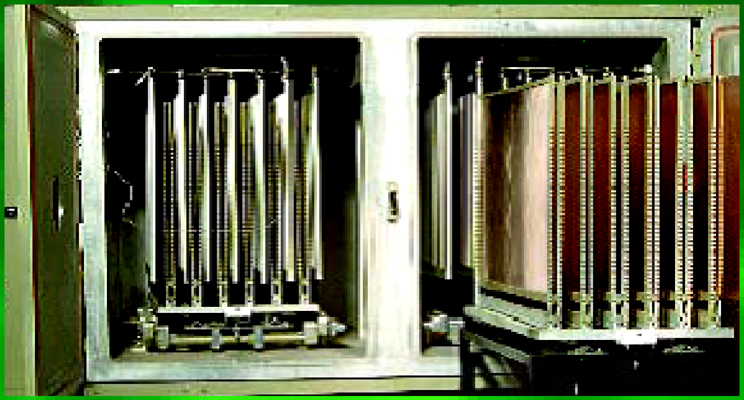
- PCBs with layer counts from one layer to 50+ layers are being produced.
- Circuit board sizes range from less than the size a fingernail to as large as a dinner table.
- Copper foil can reach thickness as thin as 1000 angstroms.
- Performance demands on PCB laminates are also increasing significantly
- Move to introduce new laminate materials that can meet these challenges.

- As a result of this trend, traditional manufacturing methods for pre-treating new generation components and removing residue for high speed production are no longer as cost-effective.
- Process flows which employ low-pressure plasma chambers has traditionally been labor-intensive in cleaning of PCBs of historical configurations.



- Low pressure levels in vacuum coating chambers allow the generation of a uniform plasma, usable for effective treatment of many surfaces.

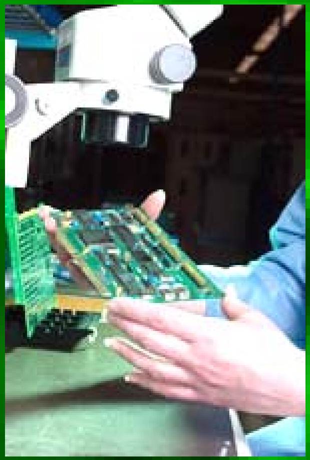
- Although the uniformity of the plasma allows for high treatment levels, these applications require cycle times which may not meet new equations for worldwide competitiveness.

- **Development of high thermal resistance PCB materials with smaller geometries.**
- **Multilayer PCBs with high-density interconnects require designs with finer pitch, and the use of new material technologies with high yield potential.**
- **Laminates based on cyanate esters, allylated polyphenylene ethers, and BT-epoxy/tetrafunctional epoxy systems may resolve coefficient of thermal expansion and speed issues.**
- **New impasses to productivity can arise during the board manufacturing process where the use of traditional processes is limited.**

Examples

- Chemical cleaning with high pH permanganate solutions is limited due to the inability of the fluid to fully penetrate the small vias found in multilayer PCBs.
- Wet chemistry approaches which involve acid etching have difficulties etching polyimide dielectric materials.

- Complex PCB constructions with increasing layers and circuit densities benefit from plasma treatment for:
  - Descum
  - Desmear
  - Removal of carbon-based organics
  - PTFE activation
  - Surface preparation



- Vacuum plasma processing of boards with high aspect ration holes and various via configurations have been historically sufficient.
- Although consumption costs are moderate, initial capital costs can be substantial when increased processing capacities are needed.

What is Atmospheric Plasma Treatment?

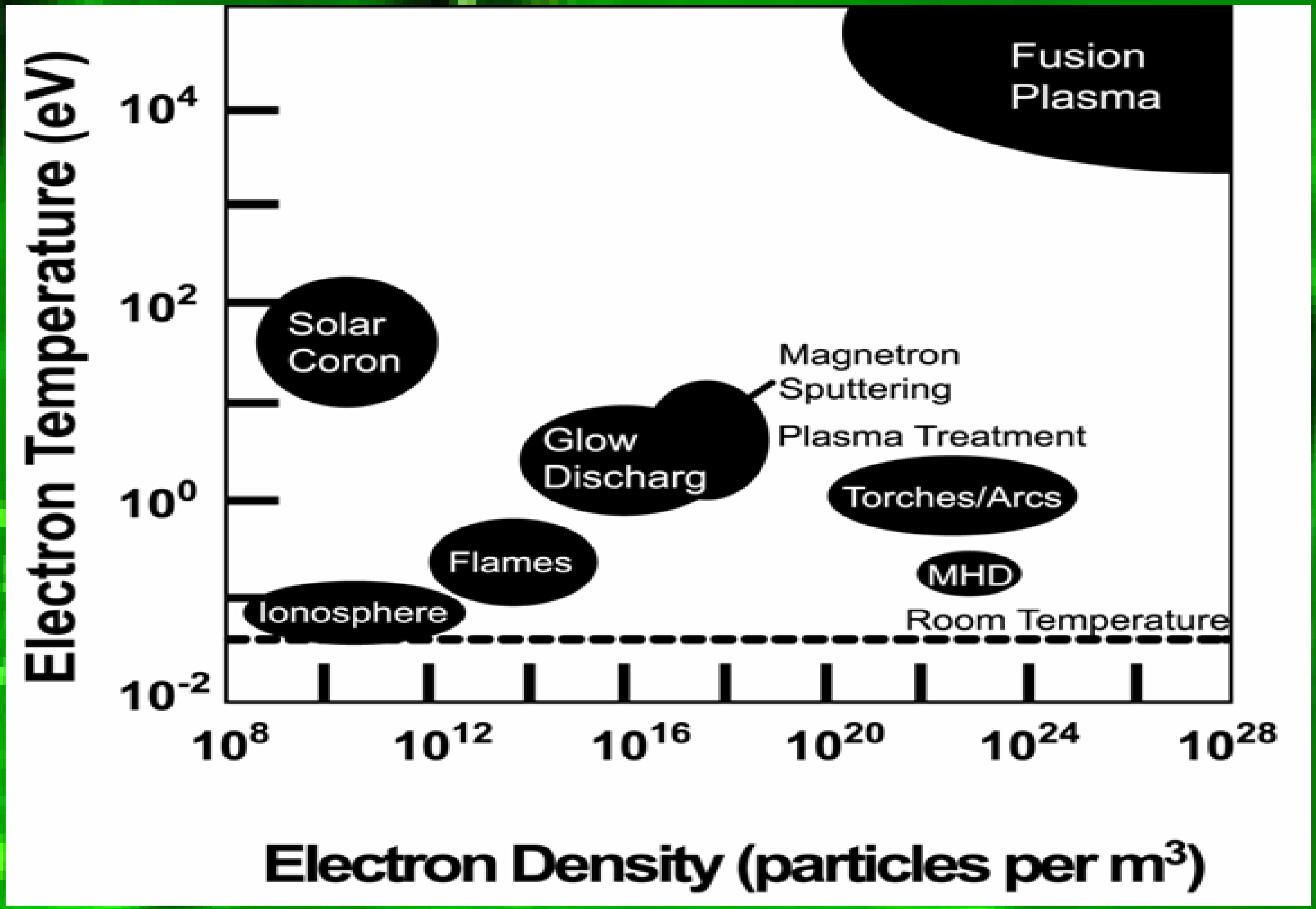
Atmospheric Plasma

Plasma Discharge With Gas and Substrate in the Gap
(Photo taken at 1/1000 of a second)

Atmospheric Plasma what is it?

- Like Corona, Atmospheric Plasma is the electrical ionization of a gas.
- Atmospheric Plasma creates a smooth, undifferentiated cloud of ionized gas (high density plasma) with no visible electrical filaments.

Plasma Densities

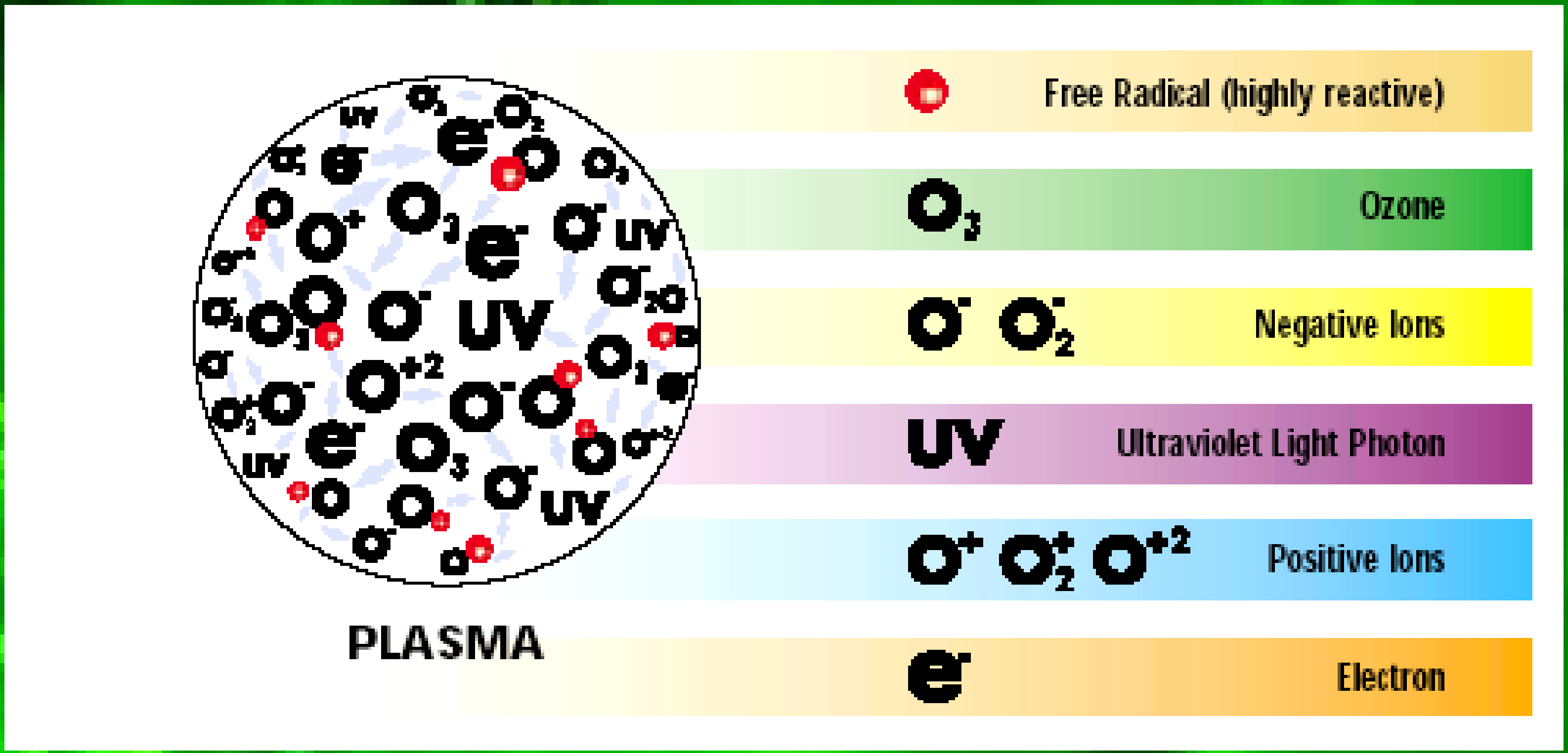


Atmospheric Plasma Treatment

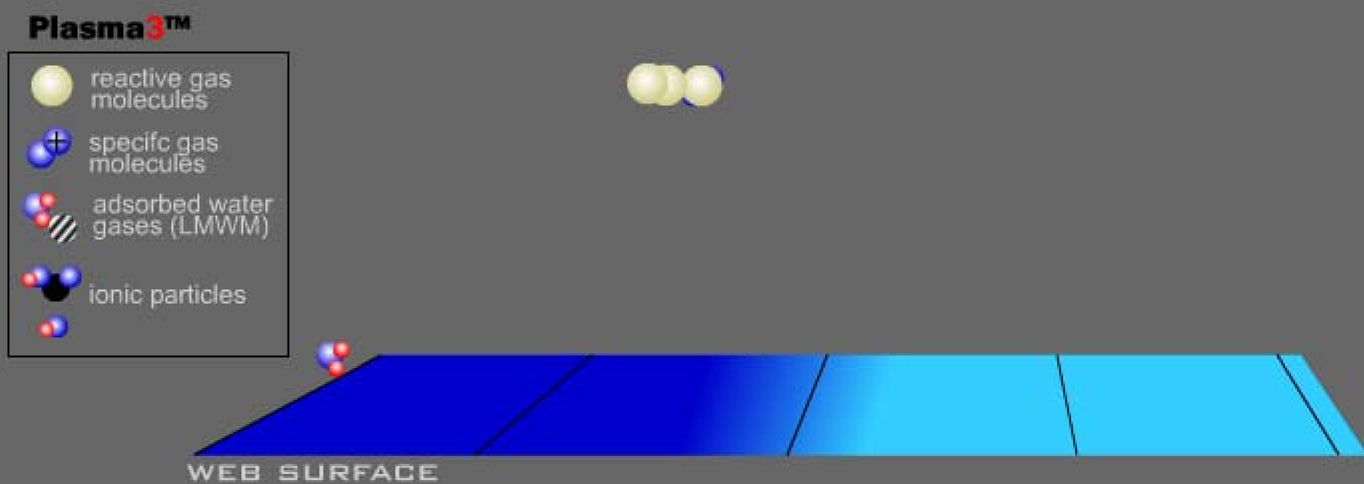
Effects of plasma on surfaces

- Electron bombardment ⇨ cross-linking
- Ion bombardment ⇨ surface etching
- Excitation of gas ⇨ chemical reactions on the surface
- UV radiation ⇨ similar to electron bombardment

Atmospheric Plasma Treatment



Atmospheric Plasma Process



HOW PLASMA FUNCTIONALIZES A SURFACE -

Reactive gas molecules are accelerated or diffuse towards the target surface under the influence of electric and/or magnetic fields. Low molecular weight materials (LMWM) such as water, adsorbed gases and polymer fragments are knocked off the surface of the film to expose a fresh, clean surface of the bulk substrate. At the same time a percentage of the reactive components of the plasma gas mixture with sufficient energy to bond to the freshly exposed bulk substrate, do so thus changing the chemistry of the substrate surface to impart the desired functionality.

Atmospheric Plasma Process

- **Can be used as a dry etch process for the removal of drill smear.**
- **The smear on the copper surface, if not removed, would prevent interconnection between it and the electroless copper which is to be plated in the hole barrel.**
- **Can be used in etchback for the removal of epoxy-resin that leaves the copper interface protruding into the hole.**

Atmospheric Plasma's Role in PCB Processing

Base material

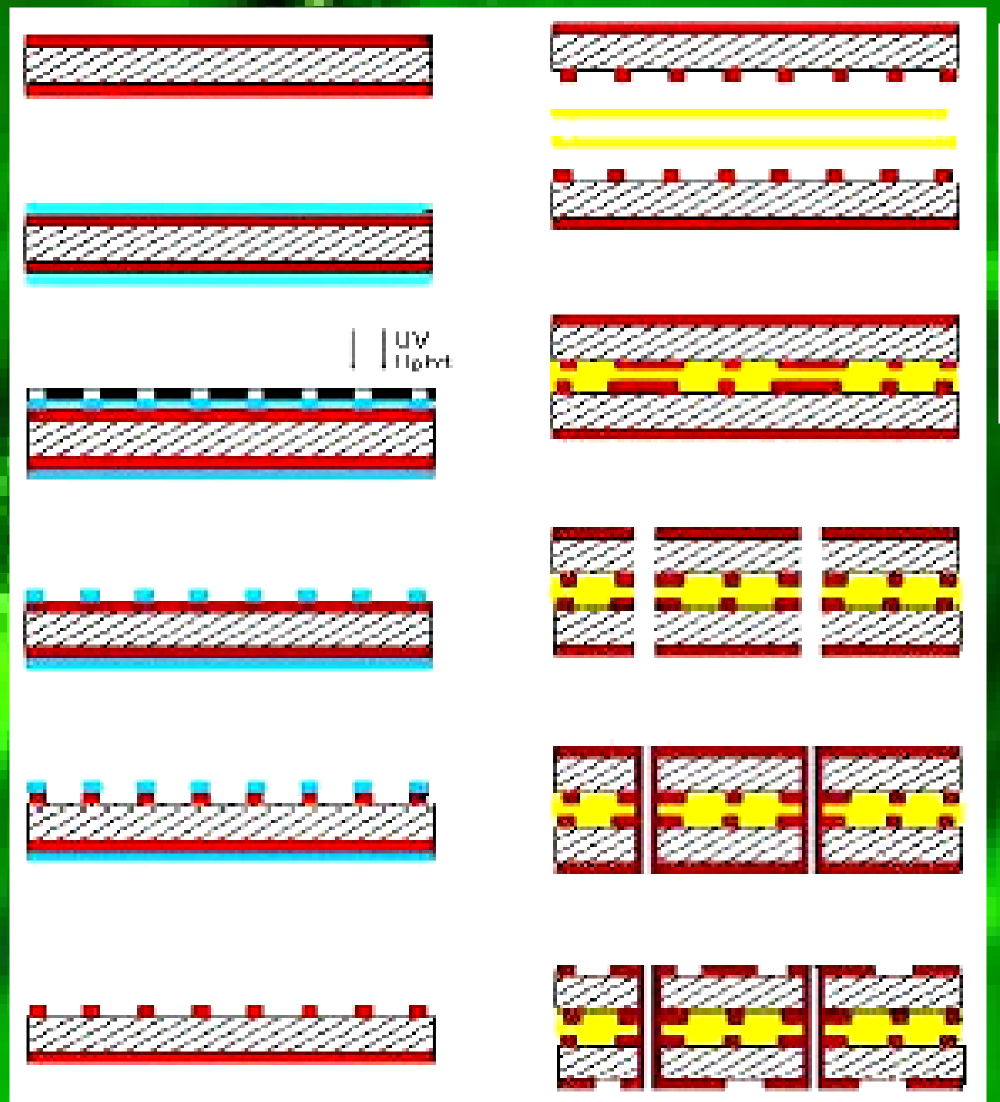
Lamination of photoresist

Image transfer (internal layers)

Photoresist Development

Etching

Stripping



Pressing

Drilling

Metallization

Image transfer (external layers)

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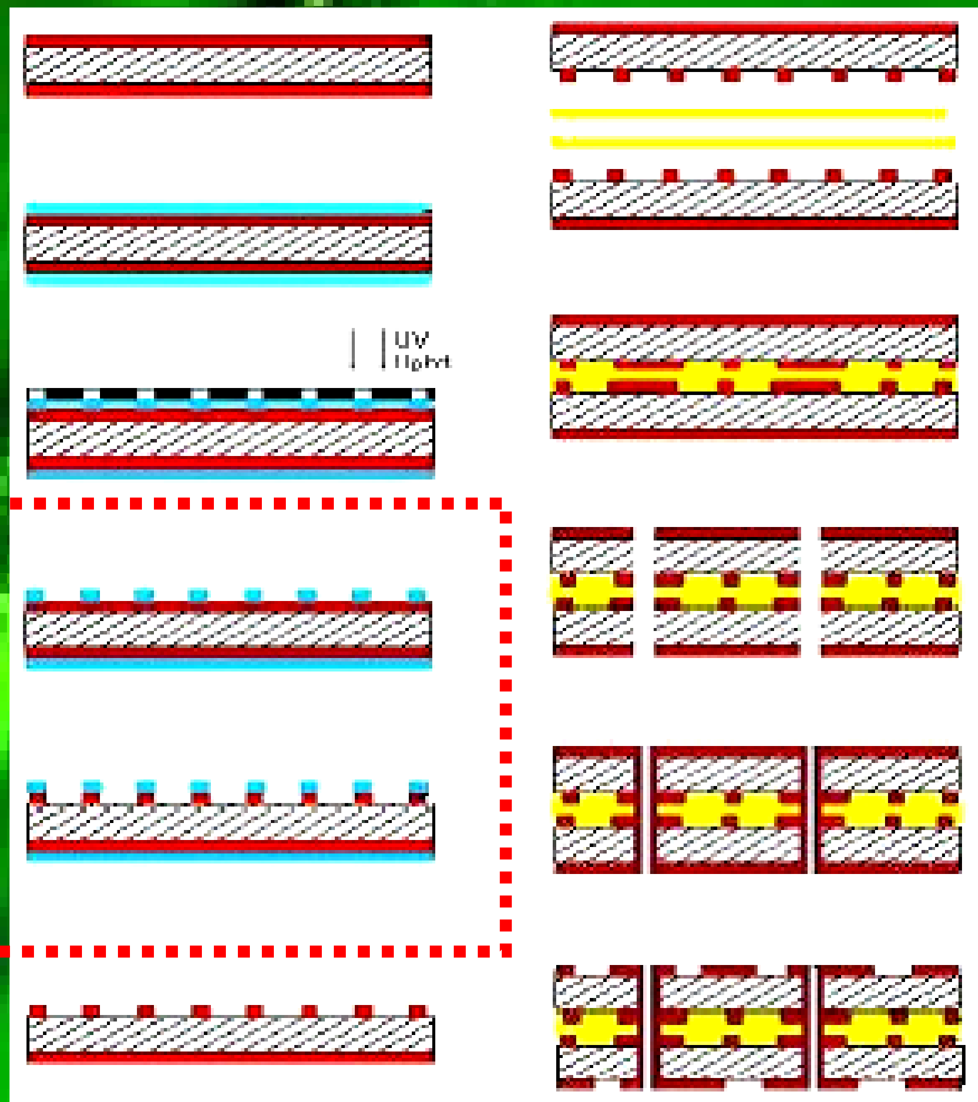

Pressing

Drilling

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Image transfer (external layers)

Atmospheric Plasma's Role in PCB Processing

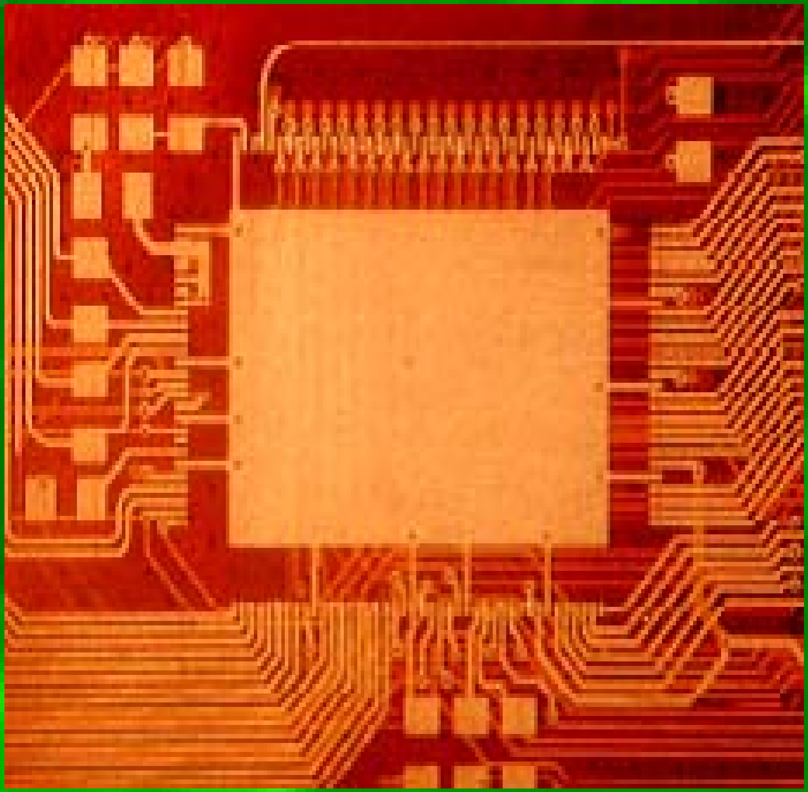
Different Materials For PCB

Dielectric matrix
- FR4, G10, Teflon, Polyimide, polyethylene, halogen free, cyanate ester.

Dielectric fiber
- Glass, Kevlar

Conductors
- Copper

Built in Heat Sink
- Cu/Invar/Cu, Cu, Al, Carbon



Atmospheric Plasma & High Throughput Photoresist Strip

Photoresists…

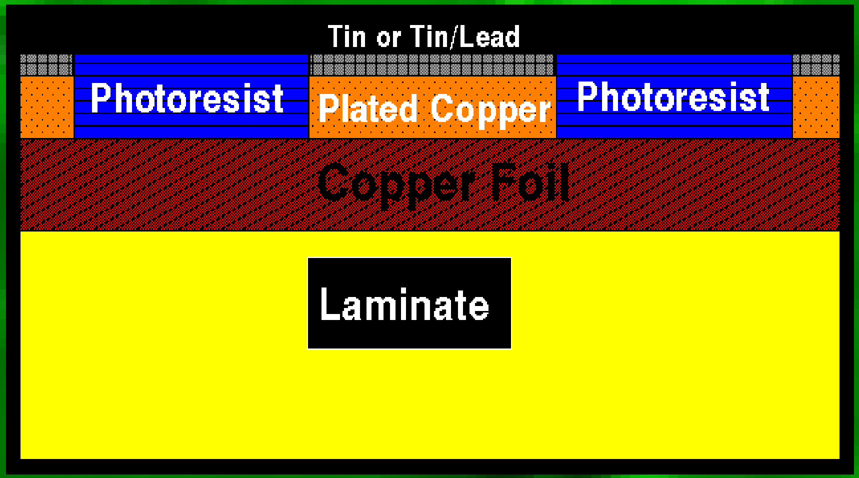
- are composed of polymers with a hydrocarbon background.

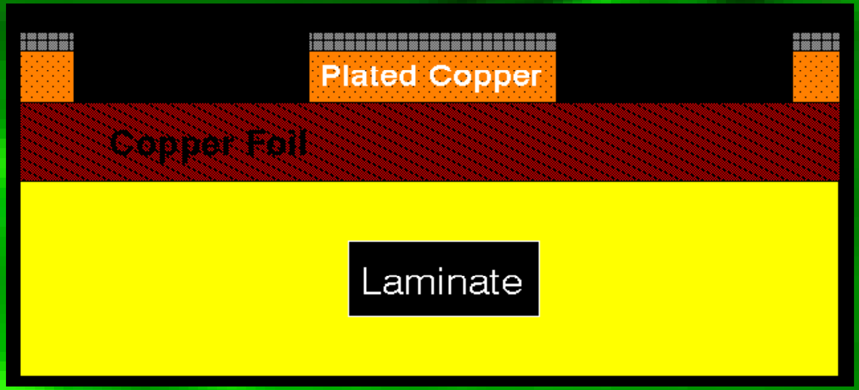
Liquid stripping approaches…

- are becoming less desirable in advanced device production due to incompatible chemistries, topological limitations and damamge caused by surface tension effects.

In IC packaging…

- Atmospheric plasma is used to clean photoresist from surfaces prior to bonding, encapsulation, and die attach.





Atmospheric Plasma Sheet PCB Processing

Gas mixtures…

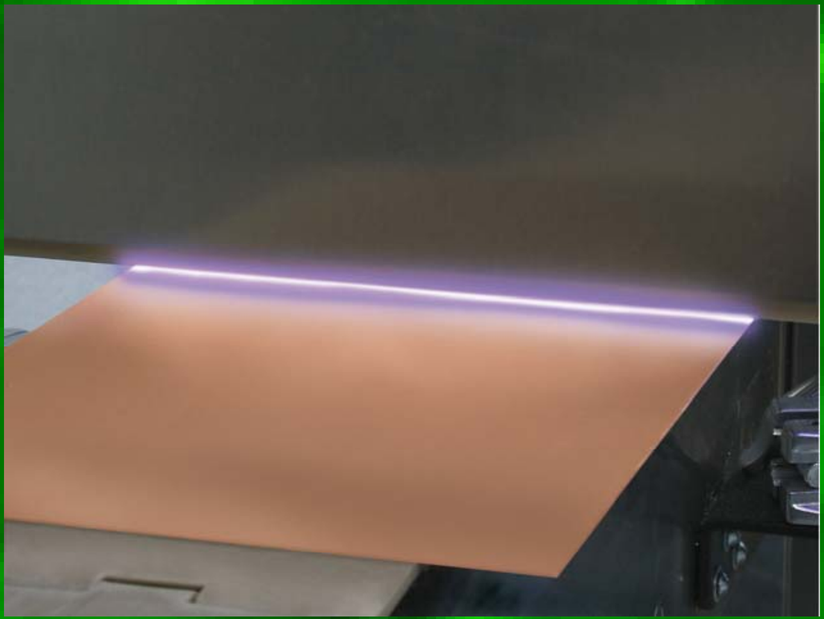
- CF4, NF3, tetrafluoromethane, or oxygen, for example, can be used for this process.

The energized mixture…

- will react with the polymer impurities and create volatile end products which are vaporized, then evacuated within an exhaust stream

Key control variables…

- are power density, speed, gas flow rate, gas mixture.



Experimental Evidence

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Experimental Evidence

- Non-thermal atmospheric plasma glow discharge system employed to clean resist layer created higher levels of hydrophilicity as levels of reactive oxygen were increased relative to carrier gas.
- Contact angles below five percent were measured, indicating that low molecular weight organics were effectively removed prior to lamination.
- High density, RF-generated plasma field was contained within a continuous design, allowing continuous conveyance of either sheet or web forms of PCB construction layers.
- Increasing power density gas chemistry flow rates will directly enable increased processing speeds.
- Alternative to traditional batch (chambered) plasma cleaning systems which advocate a two stage treatment process which can take up to one hour of cycle time per batch.

Atmospheric Plasma System - Key Benefits

- Sustained at atmospheric pressure plasma that permits surface cleaning of PCB on a continuous sheet & web handling basis
- The atmospheric plasma process allows treatment using a broad range of reactive gases.
- Web and sheet processing speeds in excess of current PCB processing speeds can be achieved.
- Atmospheric plasma system are removing residues of contaminants from sensitive surfaces without damaging them to increase yields.
- Dry process relative to wet chemistry demear, so possible to eliminate chemical requisitions and disposals in some processes.

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