

Plasma Polymerization: A Versatile and Attractive Process for Conformal Coating

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ABSTRACT

The use of plasma processing in the manufacture of electronics is growing as we discover more and more applications for this technology. It is now common for plasma etching and cleaning to be used in multiple stages of the electronics manufacturing process. The introduction of new plasma polymerization methods and equipment has added new possibilities and applications for plasma.

Plasma polymerization is a unique and exciting new tool for our industry. Plasma polymerization is a simple, one step process that can be used to apply a thin, uniform film as a protective coating which requires no curing or the use of any solvents. The chemical structure and properties of the coating can easily be tailored to the requirements of the application by selection of the appropriate precursors and processing conditions. The protective coatings that can be deposited using plasma polymerization represent an opportunity for the industry to deliver new, more reliable products to the market.

This paper will discuss the plasma coating process and the equipment used. The application of this type of coating process to printed circuit boards and electronic assemblies and the results of tests to demonstrate the protection offered by these coatings will also be presented.

Keywords: Conformal coating, plasma coating

INTRODUCTION

The function of a conformal coating is to protect electronic assemblies from damage caused by exposure to the environment. These coatings are generally applied as a liquid, using manual techniques such as brush coating, spray coating or dip coating. Spray coating, needle dispense and dip coating can also be automated using robots to apply the conformal coating in a more controlled manner. All of these techniques can be time and labour intensive, and generally require that sensitive areas of the assembly, such as connectors and RF components, be masked off prior to coating to prevent the liquid conformal coating materials from coming into contact with these areas. After application of the coating, these materials generally need to be cured to harden, typically using either UV exposure or heat, or some combination of the two. This step adds more time to the coating process, and can emit unpleasant and potentially harmful solvents as the coatings dry. A new method of applying a thin, protective coating to electronics would be highly desirable if it could deliver the required level of protection from the environment while eliminating the unwanted process steps. Plasma polymerization offers such a solution.

PLASMA POLYMERIZATION

Plasma polymerization is defined as the formation of polymeric materials under the influence of plasma conditions¹. The deposition of solid coatings under plasma conditions has been well studied since the 1960s, with a very wide range of materials now accessible². The solid materials deposited under plasma conditions are generally referred to as plasma polymers, but they are unique and distinct from traditional polymers in that they lack the repeat structure that typically defines a polymer chain. Additionally the materials tend to be highly cross linked, and not soluble in any chemical solvents. One of the advantages of plasma polymers is the fact that they tend to deposit as thin, pin hole free films in a relatively simple one step process. This property is key in the application of plasma polymers as conformal coatings for electronics. Figure 1 shows the chemical structures of traditional straight chain PTFE polymer and a plasma deposited fluoropolymer. The plasma polymer is composed of a mixture of C-F and C-C bonds, and is highly cross linked while the PTFE material consists solely of CF₂ repeat units.

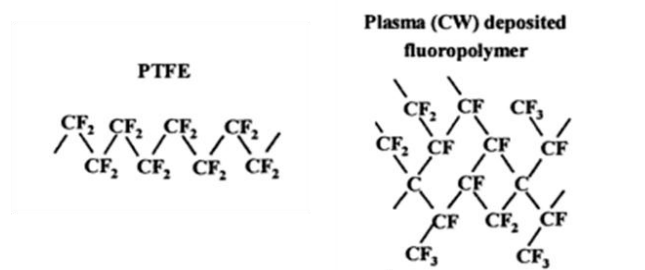


Figure 1. Chemical structures of a traditional linear PTFE polymer and a plasma deposited fluoropolymer³.

Another key property of plasma polymerization is that the coatings tend to deposit in a very uniform, conformal nature on all surfaces in the plasma system which are exposed to the active plasma gas. This means that it is possible to easily coat around corners and edges of components, which can be problematic with traditional liquid coating methods as the liquids can tend to run off of these sharp edges. Plasma polymers also tend to be very adherent, and to form good bonds with the substrates being coated. This can eliminate problems such as coating delamination during high or low temperature exposure.

PLASMA POLYMERIZATION MECHANISM AND EQUIPMENT

The mechanism of plasma polymerization is very complex. The high energy ionization which takes place in the plasma system breaks the precursor gas into ions, free electrons, radicals and neutral fragments, all of which can be involved in the recombination of these fragments into plasma polymers on the surface of a substrate. The exact chemistry of the resulting coating is dependent on the chemistry of the precursor along with a host of parameters specific to the plasma deposition system such as chamber design, electrode configuration, RF frequency and power, pressure and flow rate of the precursor.

There are a range of plasma systems in the market which are suitable for use as plasma polymerization coaters. Figure 2 shows 3 such systems manufactured by Nordson March for Semblant Ltd, which vary in size and can be useful for anything from small volume R&D work to high volume manufacturing. These systems have been specifically engineered to run optimized coating processes and to convert both gaseous and liquid precursors into plasma polymerized coatings. The small volume system has an internal volume of 4.5 cubic feet, the medium volume system has an internal volume of 15.5 cubic feet, and the high volume manufacturing system has an internal volume of more than 30 cubic feet.



Figure 2. Examples of typical Plasma Deposition systems suitable for conformal coating. (A) Small volume / R&D system, (B) medium volume system and (C) high volume manufacturing plasma system.

EXAMPLE COATING PROCESS

The coating process used in plasma polymerization is typically a simple, one step process. Samples are placed into a plasma chamber using appropriate racking such that all important surfaces will be exposed to the active plasma gas. The plasma chamber is then pumped down to a vacuum level on the order of 10's to 100's of mTorr depending the specific process. The precursor material is then introduced to the plasma chamber as a gas. This precursor may be a gas at normal atmospheric

conditions, such as some hydrocarbon, fluorocarbon and amine gases, or it may be a liquid that has been converted to gas. This conversion can be achieved using methods as simple as pulling a vacuum on the headspace of a high vapour pressure liquid, passing a carrier gas through the liquid and then introducing the precursor-saturated carrier gas to the chamber, or as complex as direct liquid injection via an atomization process for liquids which have a very low vapour pressure.

Once the flow of the precursor into the chamber has stabilized, the RF generator is switched on and the precursor vapour is ionized into a gas plasma. When run at the appropriate conditions, the precursor will then deposit a coating on the surface of the samples and the thickness of the coating can be controlled by adjusting the length of time that the process is allowed to run. After the desired coating thickness has been achieved, the RF generator is switched off, and the precursor gas purged from the plasma chamber. The chamber is then brought back to atmospheric pressure, and the coated samples are removed from the system. No further drying or curing of the samples is required. This process is illustrated in Figure 3.

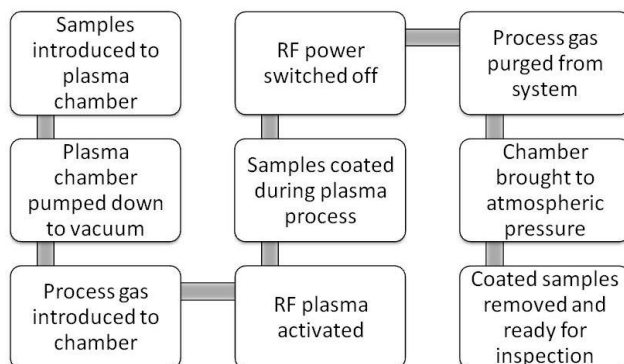


Figure 3. (A) Samples are placed in the plasma chamber. (B) The plasma chamber is evacuated. (C) The precursor gas is introduced and the plasma activated. (D) After the desired thickness has been deposited, the chamber is brought to atmosphere and the coated samples can be removed.

PLASMA DEPOSITED CONFORMAL COATINGS

As described above, the plasma polymerization process can be used to deposit a wide range of materials. These include simple hydrocarbons, more complex hydrocarbons such as acrylates and vinyl monomers, fluoropolymers and other halo-hydrocarbons as well as silicones and other silicon containing materials.

The plasma polymer coatings can range in thickness from a few 10's of nanometers to several micrometers depending on the application requirements. The thickness of the coating can be measured using physical techniques such as surface profilometry or atomic force microscopy, or it can be measured optically using ellipsometry or reflectometry. Figure 4 shows the thickness of 2 coatings as measured by a Dektak surface profilometer. In this case the coating thicknesses are approximately 300nm and 600nm.

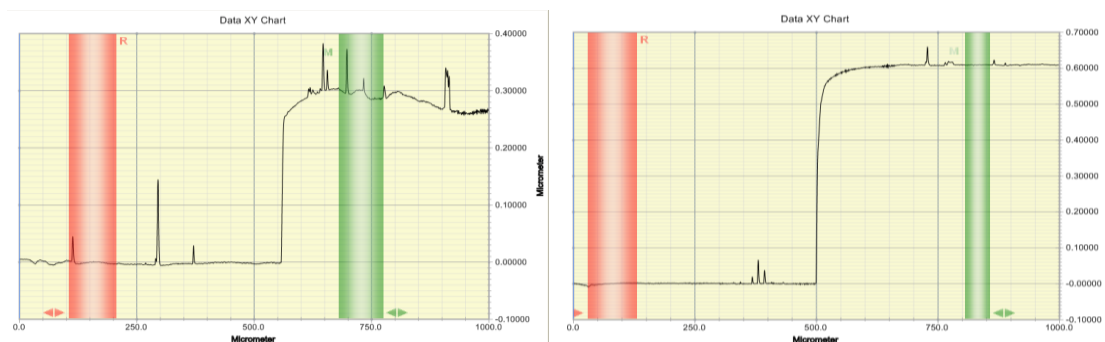


Figure 4. Dektak surface profilometer measurements of 2 plasma deposited conformal coatings showing thickness of (A) 300nm and (B) 600nm.

It is possible to image the coatings deposited in the plasma using high resolution optical microscopy and by scanning electron microscopy (SEM). Electronic assemblies have been coated using this plasma polymerization process and then potted and microsectioned in order to inspect the conformal nature of the coating. Figure 5 shows the presence of a thin, conformal coating across the surface of a soldered pad on a PCB assembly. The thin coating can be seen to follow the contours of the metal along the edge of the pad, and then continues along the surface of the PCB and over the soldermask. The lighting and contrast in the image have been modified and enhanced to highlight the presence of the thin film. The coating thickness in this case was approximately 1.5 micrometers.

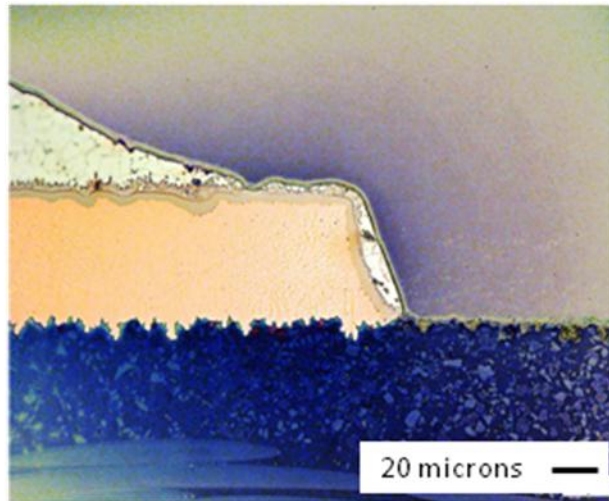


Figure 5. Optical micrograph of a cross section of a soldered pad on a PCB which has been coated with 1500nm conformal coating using plasma polymerization.

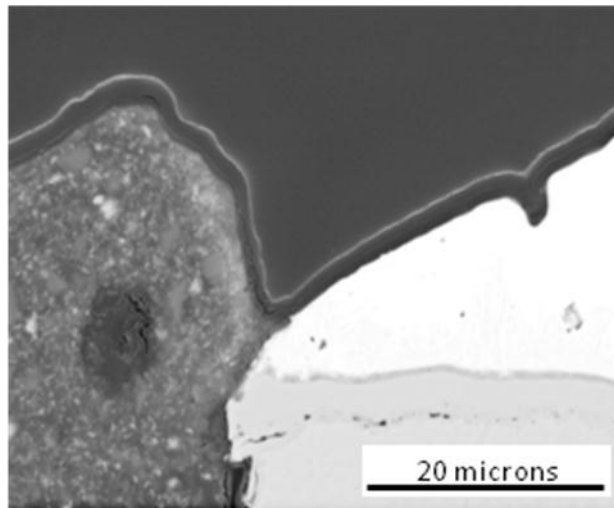


Figure 6. SEM micrograph of a cross section of a soldered pad on a PCB which has been coated with 1500nm conformal coating using plasma polymerization.

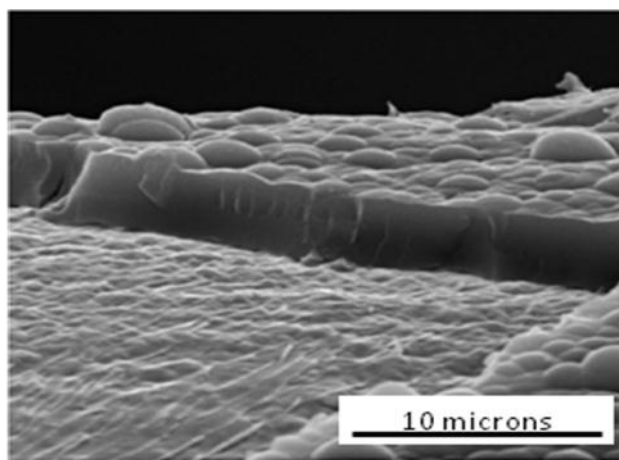


Figure 7. SEM micrograph of a section of a 1500nm conformal coating using plasma polymerization.

A higher resolution scanning electron micrograph (Figure 6) again shows the uniformity of the coating coverage and the conformal nature of the coating as it covers the metal pad and the adjacent soldermask. It is important to note how the coating easily covered the complex contours of the interface between the solder pad and the soldermask. The coating replicated the bumps in the surface of both materials and even filled in a small divet in the solder. The final SEM micrograph (Figure 7) details a section of the surface of a sample where the coating has been removed. This image shows a coating that is relatively uniform in thickness and density, and has grown uniformly from the surface. The coating was seen to be continuous and defect free for all samples that were inspected.

CORROSION RESISTANCE OF PLASMA DEPOSITED CONFORMAL COATINGS

Previous work has shown how plasma deposited fluoropolymers can be used as board level protective coatings for PCBs⁴. These coatings have been shown to be highly effective at preventing oxidation and corrosion on PCBs exposed to harsh environments. The plasma deposited fluoropolymer coatings have been shown to be particularly effective at preventing corrosion driven by high sulphur environments. The fluoropolymers have even been shown to prevent creep corrosion when applied over an Immersion Silver surface finish which is known to be extremely susceptible to creep corrosion⁵. Figure 8 shows micrographs of immersion silver finished electronic circuits which are (A) uncoated and (B) coated using plasma polymerization after exposure to a high sulphur, high humidity environment for 7 days. The uncoated sample shows severe creep corrosion while the plasma coated sample looks pristine.

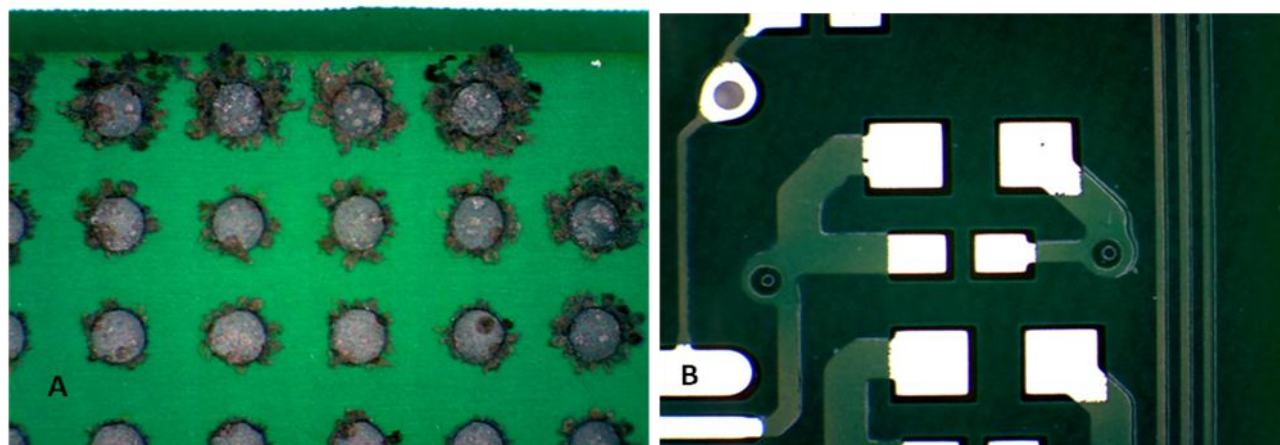


Figure 8. Optical micrographs of immersion silver finished electronic circuits which are (A) uncoated and (B) coated using plasma polymerization. The uncoated samples shows severe creep corrosion while the plasma coated sample looks pristine.

An important characteristic of a many conformal coatings is the ability to protect the circuitry in an electronic assembly from exposure to the combination of moisture and corrosive elements when the circuit is in operation. These conditions can arise when the product is placed in a high humidity environment, if the sample is exposed to a condensing environment, or if any

water accidentally reaches the surface of the circuit. An unprotected electronic assembly can often suffer from catastrophic failure in these conditions. One failure mechanism is the growth of dendrites across the surface of the electronic assembly. These dendrites are conductive metal salts formed by the combination of water and corrosive elements on the surface, and are driven to grow by applied voltages across the circuit.

It is possible to show the impact of this dendritic growth when a circuit is exposed to tap water and a voltage is applied. There are enough salts in the tap water to set up an electrochemical cell which results in the growth of dendrites between the 2 electrodes of the circuit. In this experiment one set of samples was coated with a 1 micron thick conformal coating using plasma polymerization, while a second set of samples was left uncoated. Bare copper and Immersion Silver finished circuits were used in these sample sets. The samples were then connected to a voltage source and immersed in tap water under a microscope so that they could be observed. The first set of images in Figure 9 shows low and high magnification images of an unprotected copper circuit (left) and a copper circuit which has been coated with a plasma deposited conformal coating (right). The uncoated sample clearly shows the growth of dendrites between the electrodes, while the plasma coated sample shows no damage to the circuit.

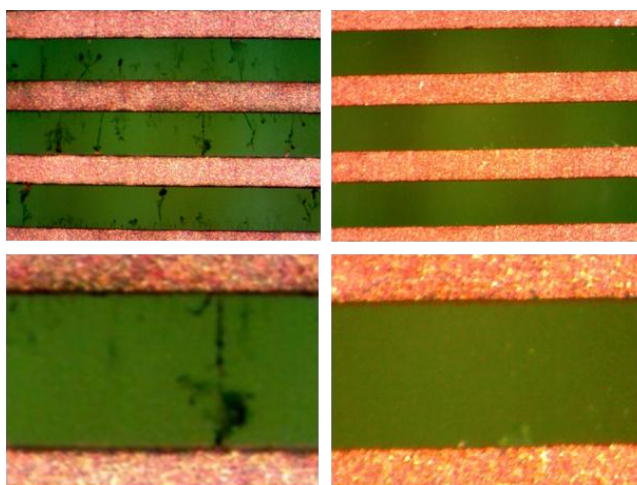


Figure 9. Low magnification and high magnification images of bare copper (left) and plasma polymer coated copper (right) after applying voltage while immersed in tap water. The uncoated samples show the presence of dendrites between the electrodes.

LIQUID IMMERSION TESTING

Liquid immersion testing has been performed to determine the ability of these coatings to provide protection to an active circuit when exposed to liquids such as water or salt spray. In this experiment a test PCB containing interdigitated comb electrodes was coated with a plasma polymerized protective coating of approximately 1.5 microns in thickness. The edge connector on the PCB was protected during coating to remove any concern over resistance due to the interface between the test sample and the test circuit. The samples were then connected in a test circuit with a voltage source set to 5V DC with a 10 KOhm resistor in parallel. The voltage drop across the resistor was measured in order to determine the current flowing through the test feature. The test vehicle is pictured below in Figure 11.

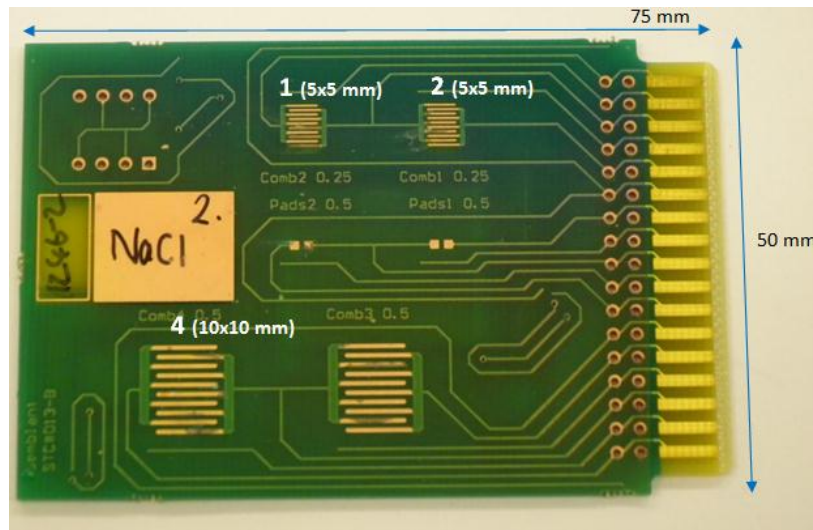


Figure 11. Test TCB used for liquid immersion testing.

Immersion testing was conducted in deionized water and in a 10g/l solution of NaCl, with the results plotted in Figures 12 and 13 below. The results for the deionized water testing show that the plasma polymer coated samples showed very little drop in measured resistance, while the uncoated samples showed a rapid drop in resistance across the test features. This resistance drop is due to current flowing through the liquid, and eventually leads to dendritic growth and shorts forming between the electrodes in the test feature. The salt solution should be a much more aggressive test solution as the concentration of ions is much higher. The results looked to be very consistent with the DI test, as the plasma polymer coated samples exhibited very little change in resistance while the uncoated samples failed almost instantly.

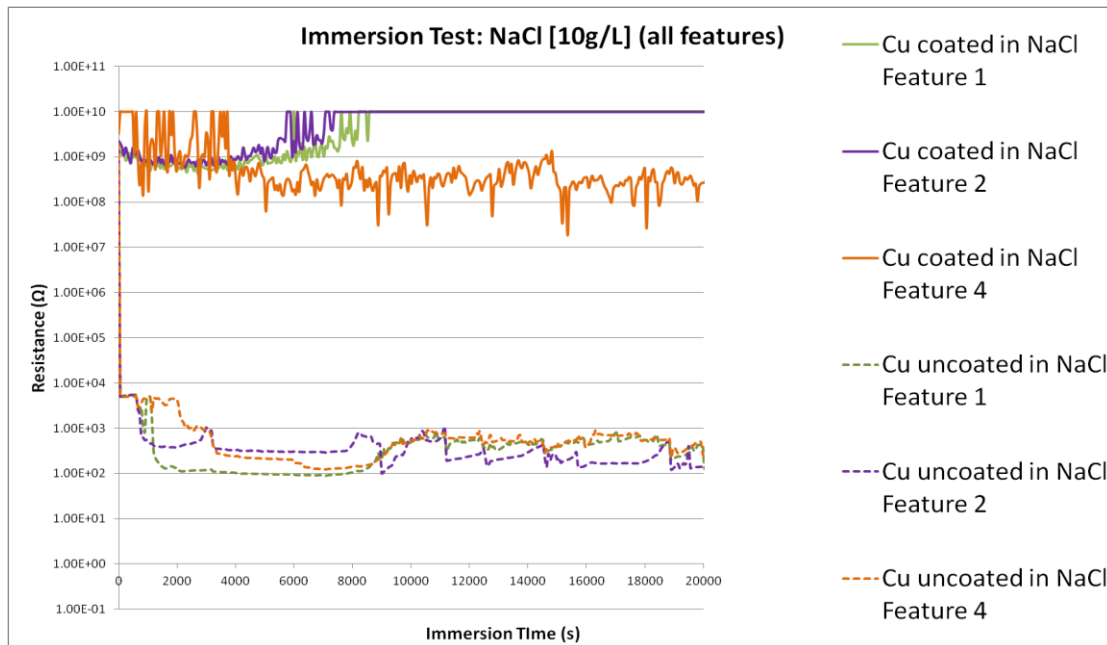


Figure 12. Immersion test data for plasma polymer coated PCB immersed in deionized water.

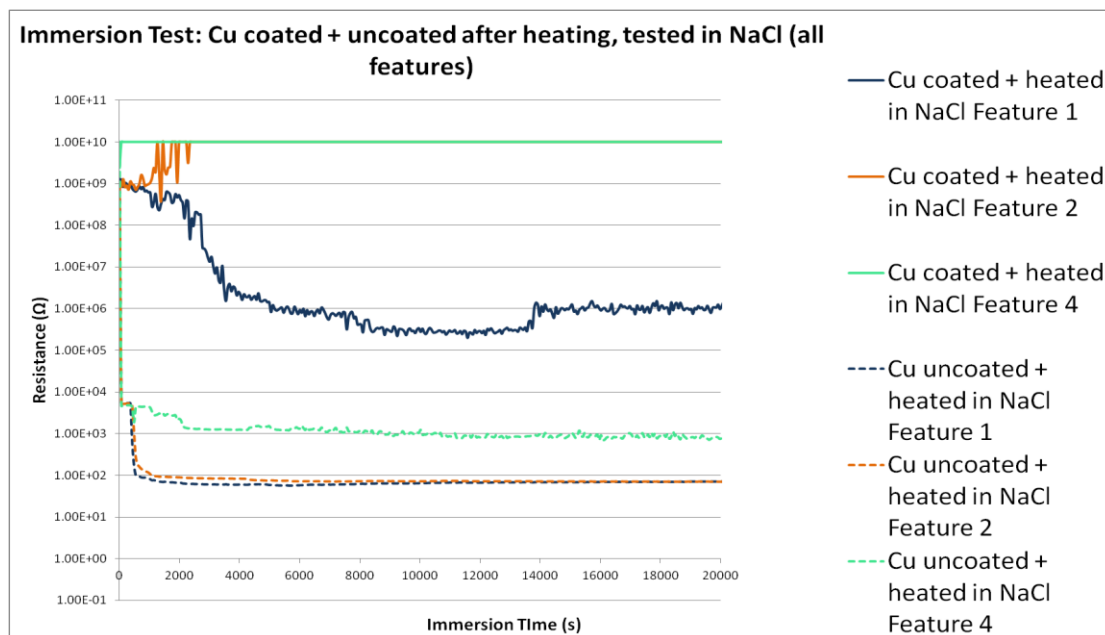


Figure 13. Immersion test data for plasma polymer coated PCB immersed in 10g/l salt solution.

CONCLUSION

Plasma deposition has been shown to be a very attractive coating method for the protection of electronic products. The deposition process itself is very simple, and can be accomplished with minimal handling or sample preparation, in some cases even eliminating the requirement for masking contacts and connectors prior to coating. Plasma polymerization offers access to an incredible range of coating materials, as virtually any material which can exist in the gas phase can be polymerized in the plasma. We expect that use of plasma polymerization for the conformal coating of electronics will enable a new generation of improved reliability electronics as the ease of use and low cost allow more and more products to be conformally coated.

ACKNOWLEDGEMENTS

We would like to acknowledge the contributions of Jim Scott for microscopy and SEM work, Randy Scheuller of DfR for creep corrosion testing and James Getty and Bob Condrashoff of Nordson March.

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- [4] von Werne, T. Ph.D., Brooks, A., Woollard, S., "Latest Developments in Surface Finishing of PCBs Using Plasma Deposition", SMTA Int'l Proceedings, 2010.
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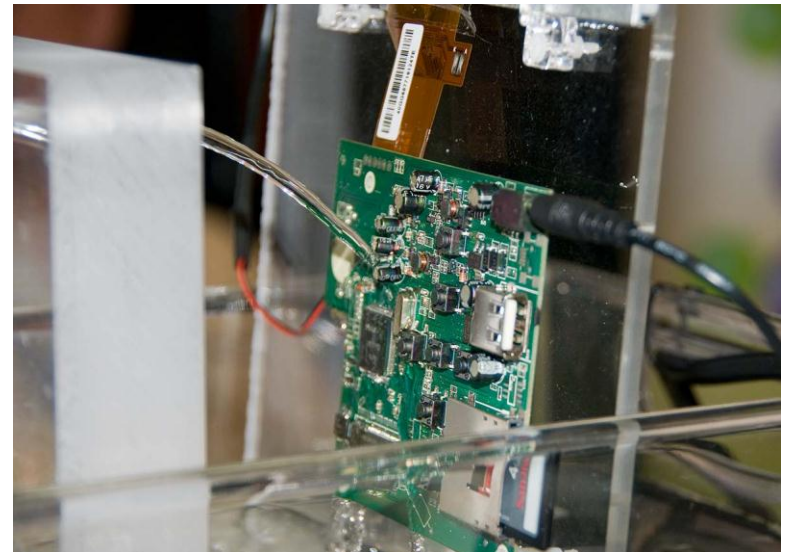
Protective Coatings for Electronics using Plasma Polymerization

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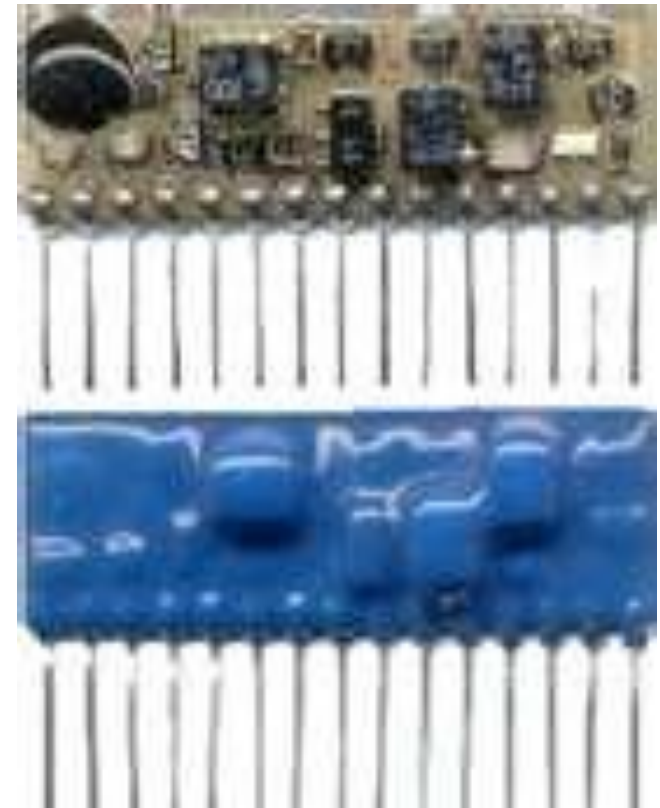
Outline/Agenda

- Introduction
- Plasma Polymerization
- Coating Characterization
- Test results
- Conclusions
- Q & A



Introduction to Conformal Coating

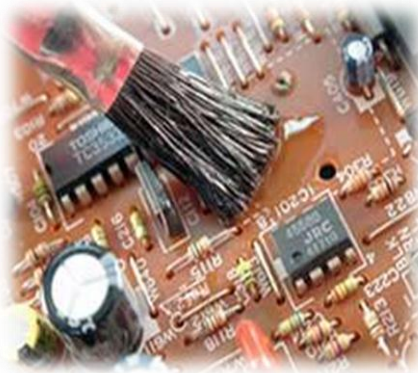
- Conformal coating is a protective chemical coating or polymer film several μm thick that 'conforms' to the circuit board topology.
- Its purpose is to protect electronic circuits from harsh environments that may contain moisture and or chemical contaminants.
- By being electrically insulating, it maintains long-term surface insulation resistance (SIR) levels and thus ensures the operational integrity of the assembly.
- It also provides a barrier to air-borne contaminants from the operating environment, such as salt-spray, thus preventing corrosion.



Conventional Conformal Coating Techniques



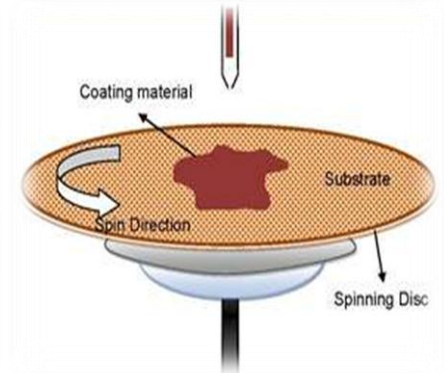
Dipping



Brushing



Spraying



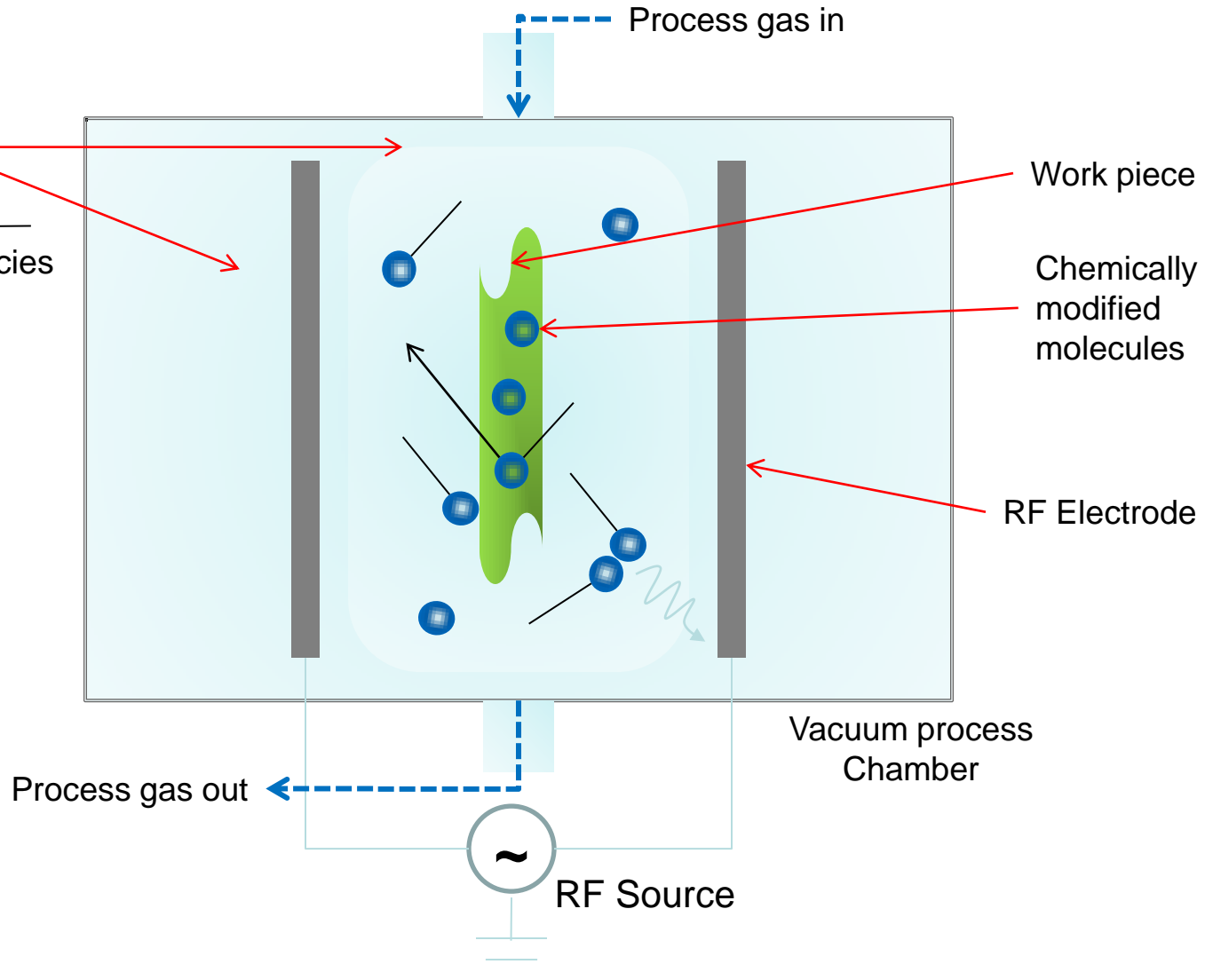
Spinning

- Drawbacks:
- Shelf life, pot life, masking, drying, curing, etc

Plasma Polymerization Coating Technique

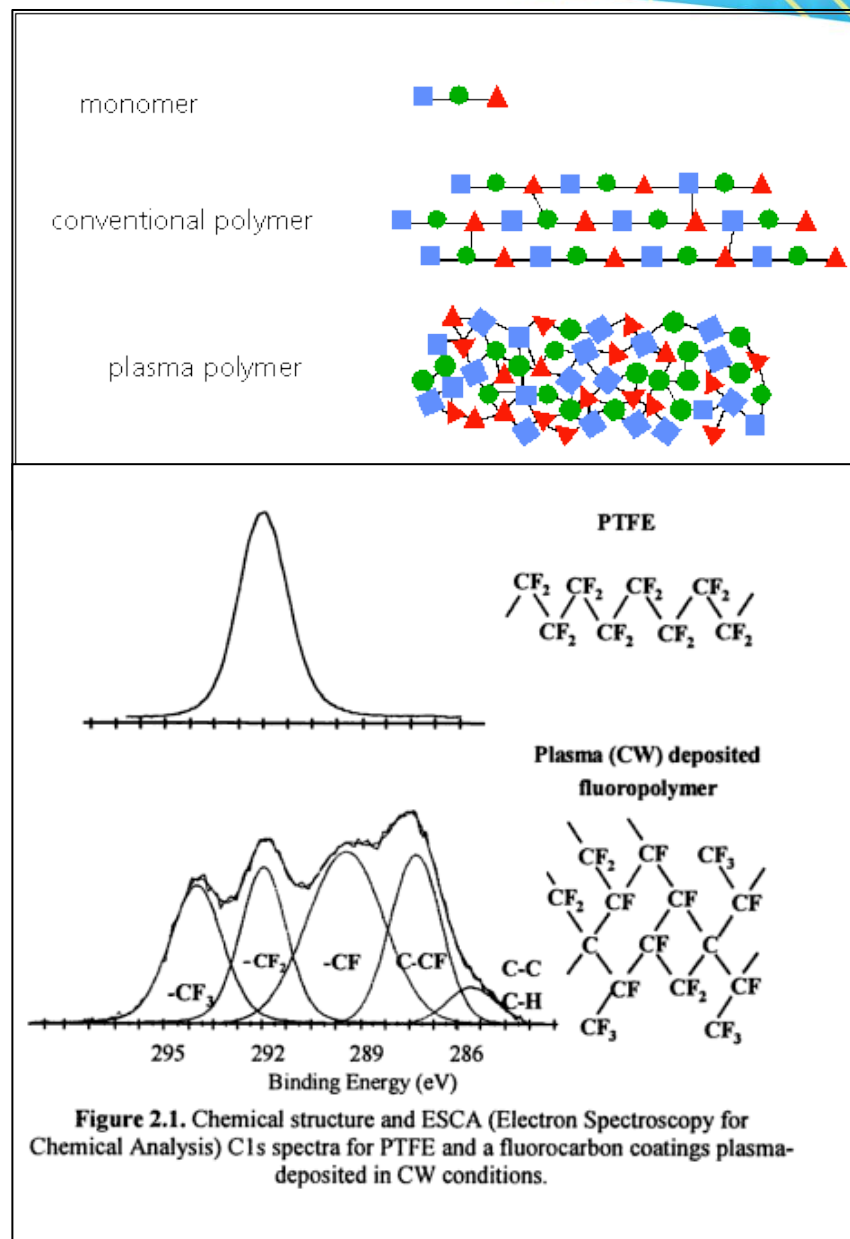
Plasma

- Excited gas species
- Atoms
- Molecules
- Ions
- Photons
- Electrons
- Free radicals
- Metastables



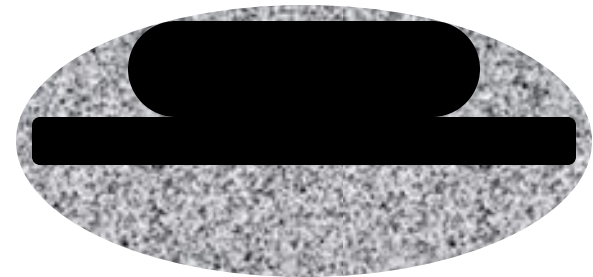
Plasma Polymerization

- Plasma polymerization
 - Virtually any organic material can be polymerized in plasma under the right conditions
 - Building blocks not original monomer material
- Conditions in the plasma chamber allow formation of unique structures
- Deposition rate dependent on several key factors:
 - Monomer composition
 - RF power
 - Plasma duty cycle
 - Monomer flow rate
 - Operating pressure
 - Temperature
 - Electrode configuration



Advantages Plasma Polymerization Coating

- Uniform dense coating
- Pinhole free
- Excellent adhesion to variety of substrates
- No curing required
- Environmentally friendly process
- Removable and reworkable
- Film chemical and physical properties can be adjusted for specific applications via easy process steps

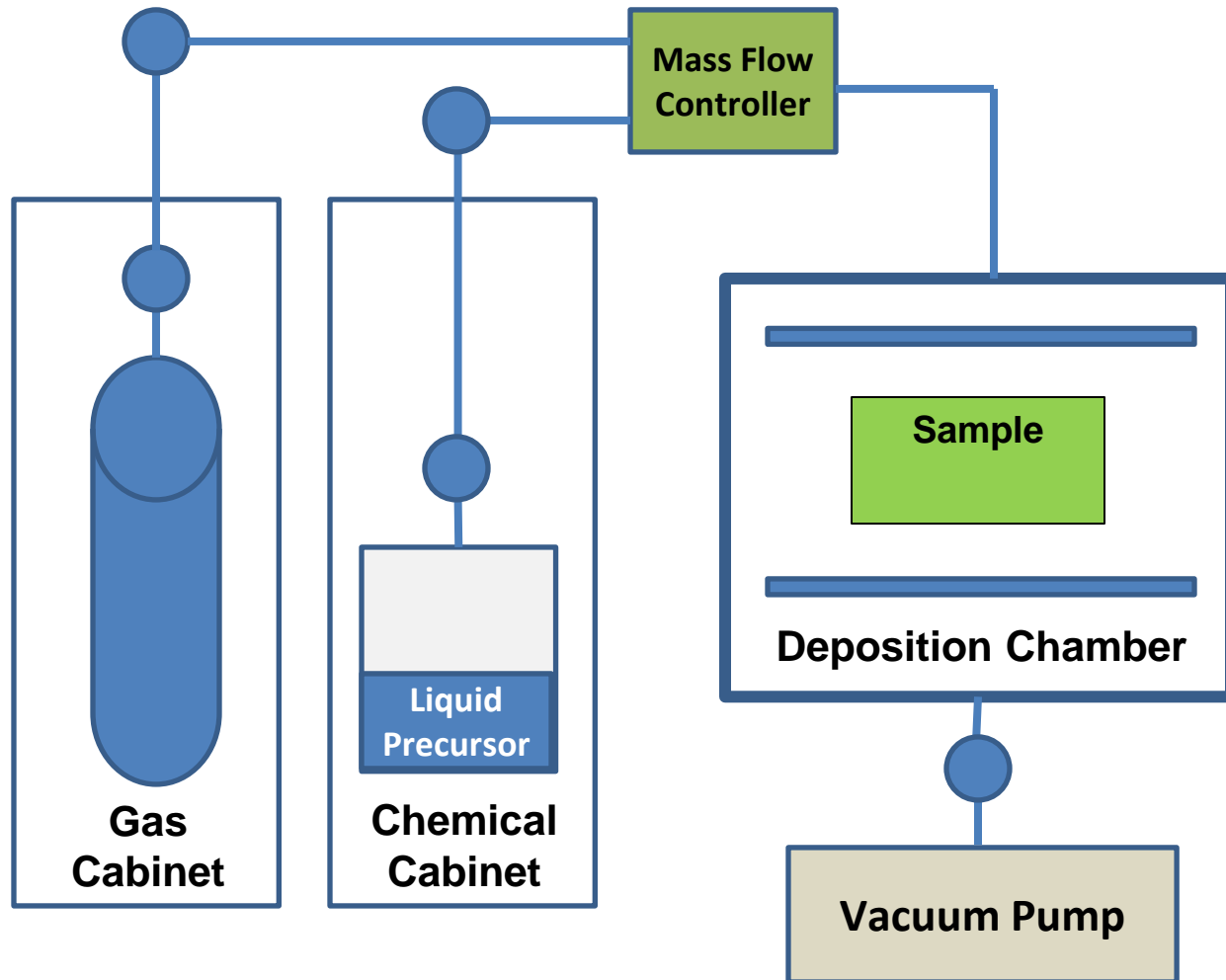


Conventional Coating
(Uneven)



Thin Film
(Uniform)

Plasma Deposition System Diagram



Commercial Plasma Deposition Systems



Low Volume /
Prototype
System



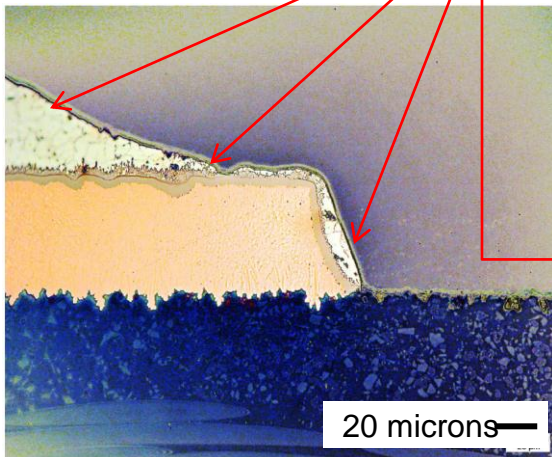
Medium Volume
System



High Volume
System

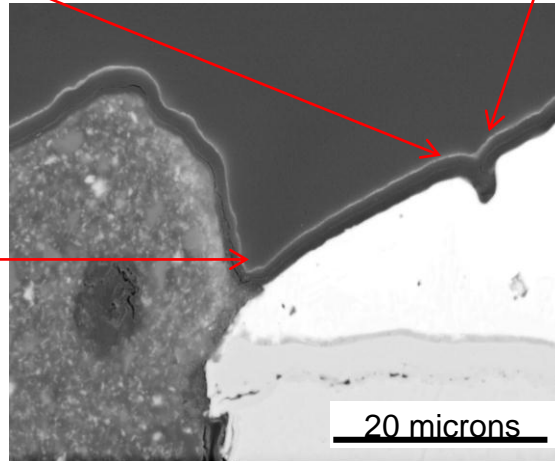
Plasma Deposited Conformal Coat Technology

High degree of
conformality

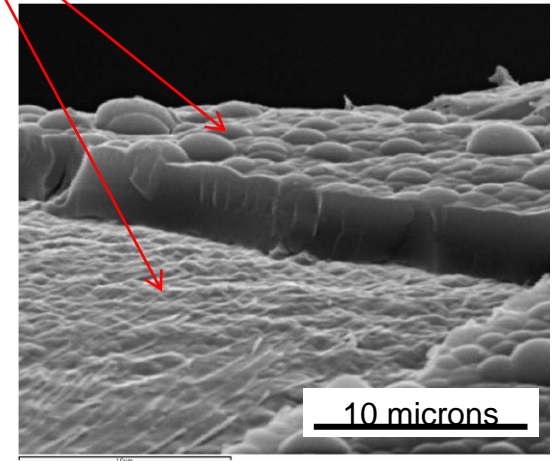


Presence of a thin conformal coating across the surface of the solder pad, and then continues along the surface of the PCB and over the soldermask.

High degree of uniformity
of thickness and density

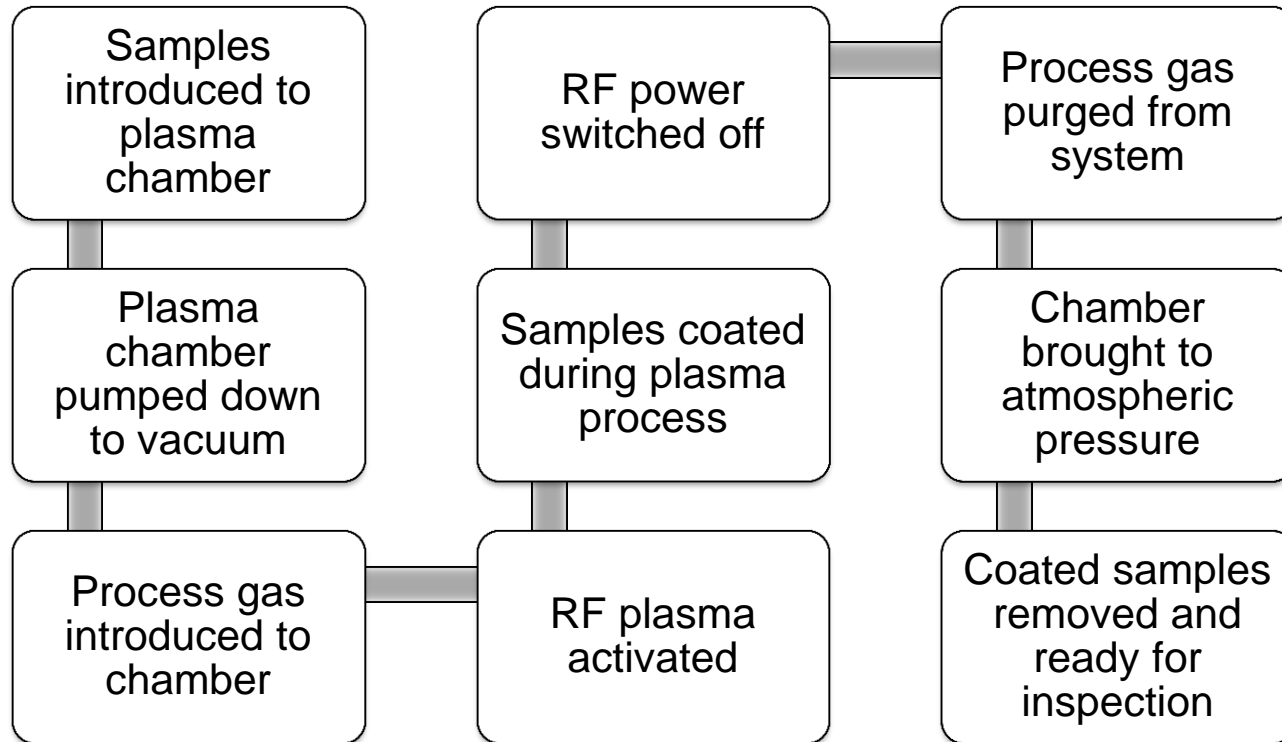


Coating uniformity being able to follow the contour of the metal and the pad while covering the bumps.



After removing the coating, the thickness uniformity and density is observed.

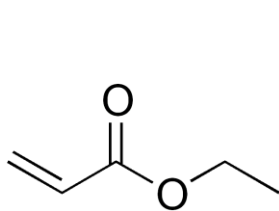
Plasma Polymerization Process Flow



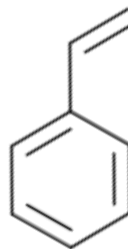
Simple --- Repeatable --- Effective --- User Friendly

Plasma Polymerization: Versatile Process

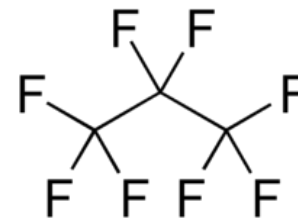
- A wide variety of precursors can be used
- Allows customization and tailoring of coating to meet application requirements



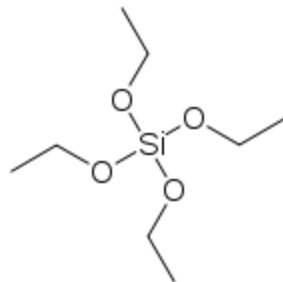
■ Acrylates and methacrylates



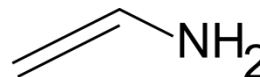
■ Vinyl monomers



■ Fluorinated monomers

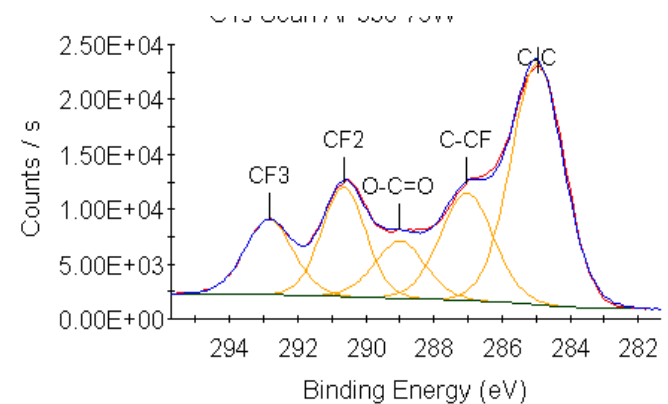
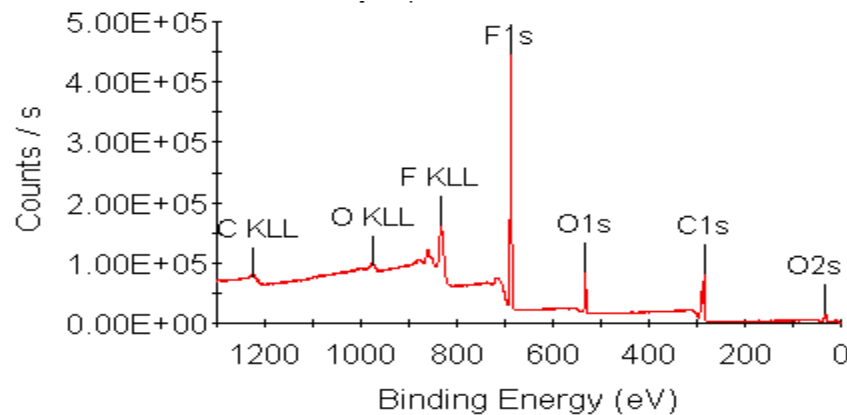
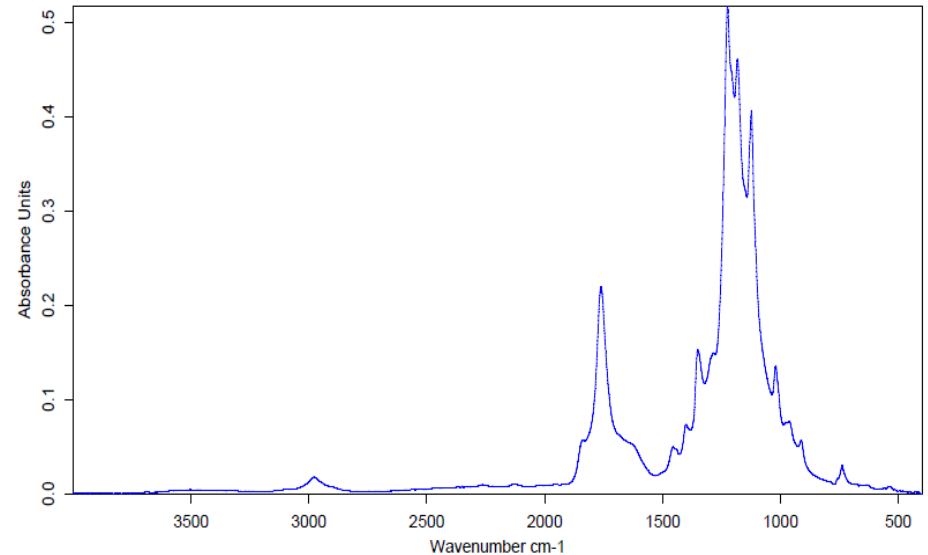
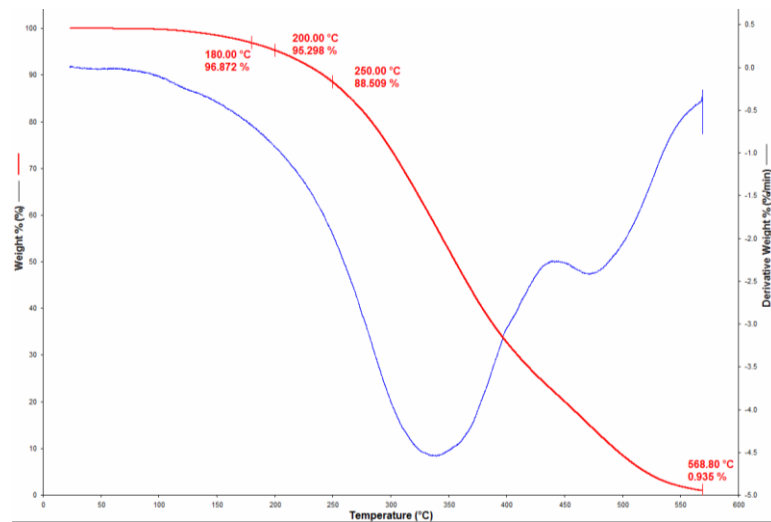


■ Silicon containing compounds



■ Nitrogen containing compounds

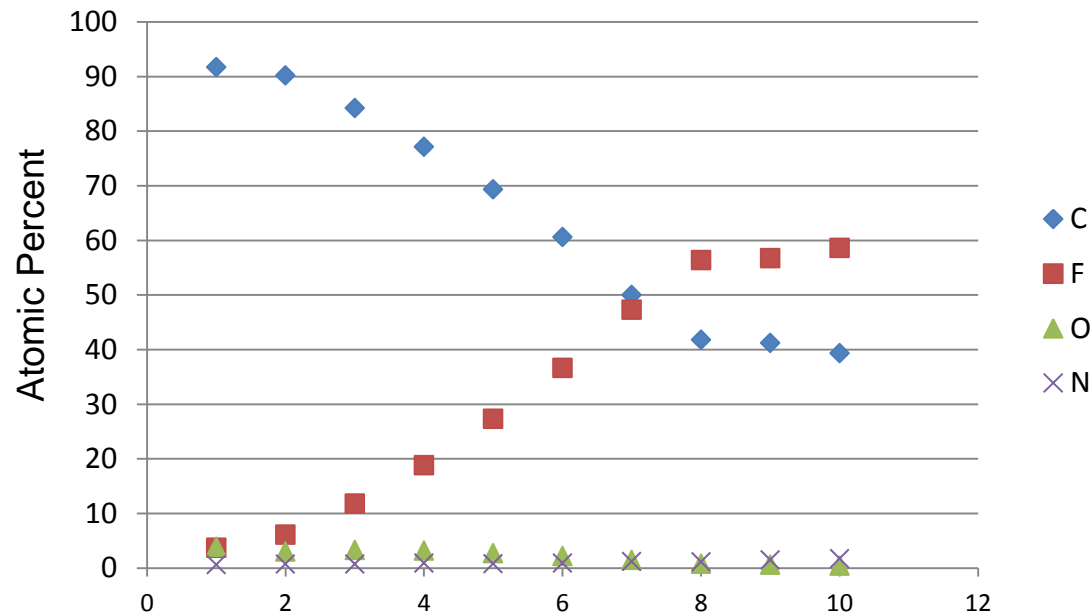
Plasma Coating Characterization



- TGA, FTIR, XPS

Plasma Polymerization: Versatile Process

- Coating composition can be varied by
 - Monomer selection
 - Blending ratio of multiple precursors



IPC 830CC Testing

Test	Specification	Test description, pass requirements
Materials	Must be free of deleterious substances	Submit MSDS, reviewed for deleterious materials
Shelf Life - Dielectric Withstanding Voltage	IPC-TM-650, Test method 2.5.7.1	1500V applied across comb pattern
Shelf Life - Moisture Insulation Resistance	IPC-TM-650, Test method 2.6.3.4	100V at 90RH, 5x10e9 minimum resistance. Test followed by repeat of DWV test.
Cure	IPC-CC-830B, Amendment 1, paragraph 3.3.3	The conformal coating shall exhibit all desired properties when applied and cured using the procedures specified by the conformal coating manufacturer.
FTIR	IPC-TM-650, Test method 2.3.42 or as agreed between user and supplier (AABUS)	FTIR Spectrum recorded and kept on file for comparison
Appearance	IPC-CC-830B, Amendment 1, paragraph 3.5.2	The coating should be smooth, free of bubbles and pinholes
Fluorescence	IPC-CC-830B, Amendment 1, paragraph 3.5.3	Conformal coating materials, except type XY, shall be fluorescent by ultra-violet illumination
Fungus Resistance	IPC-TM-650, Test method 2.6.1.1	Sample exposed to humid conditions, growth of fungus monitored.
Flexibility	IPC-TM-650, Test method 2.4.5.1	Coatings deposited on metal substrate, then put through 180 degree bend test
Flammability	UL 94 HB	Coating applied to substrate, then burned.
Dielectric Withstanding Voltage	IPC-TM-650, Test method 2.5.7.1	1500V applied across comb pattern
Moisture Insulation Resistance	IPC-TM-650, Test method 2.6.3.4	100V at 90RH, 5x10e9 minimum resistance. Test followed by repeat of DWV test.
Thermal Shock	IPC-TM-650, Test method 2.6.7.1	Samples cycled between -65 and 125C, 100x, followed by dielectric withstanding test.
Temperature and humidity Aging (Hydrolytic Stability)	IPC-TM-650, Test method 2.6.11.1	85C/95%RH for 120 days, no change to properties of coating.

MIR Testing

- Tested to IPC TM-650 2.6.3.4
- Moisture and Insulation Resistance, Conformal Coat
- 20 cycles:
 - Temp: 20-65° C
 - Humidity: 83-95%

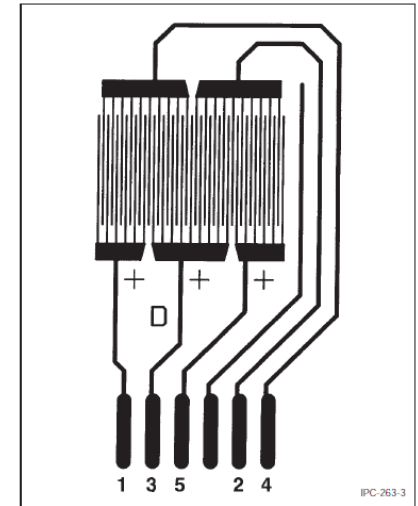


Figure 3 Typical "Comb Pattern" (from IPC-B-25A)

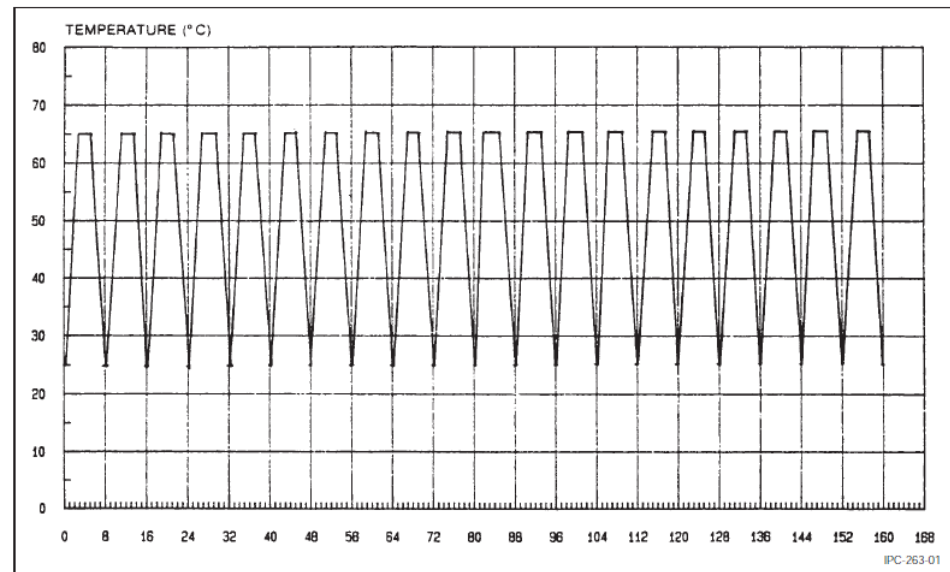


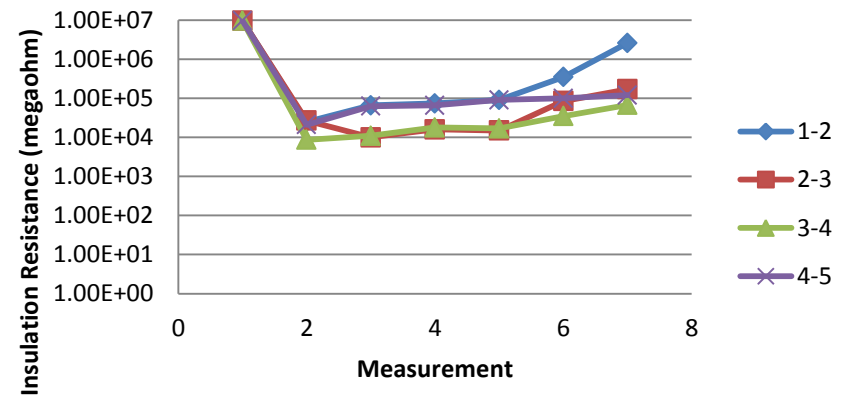
Figure 1 Moisture and Insulation Resistance Test Graph

MIR Testing

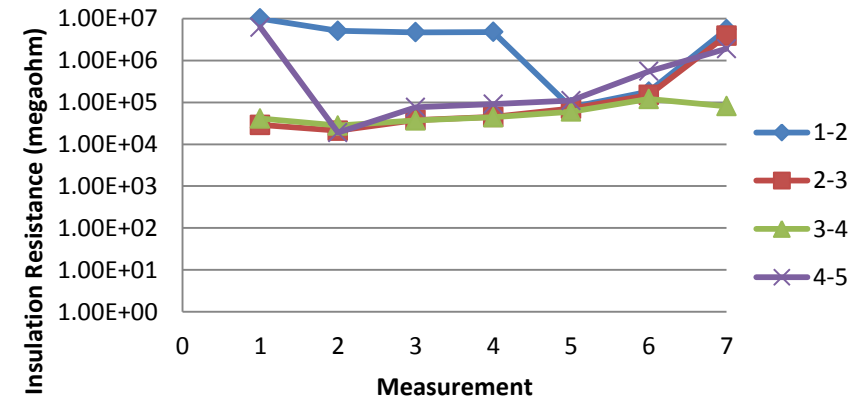
Plasma Coating 1	Test points			
	1-2	2-3	3-4	4-5
Initial	9.80E+06	9.80E+06	9.80E+06	9.80E+06
1st Cycle	2.50E+04	2.70E+04	8.70E+03	2.10E+04
4th Cycle	6.60E+04	1.00E+04	1.10E+04	6.30E+04
7th Cycle	7.40E+04	1.60E+04	1.80E+04	6.60E+04
10th Cycle	9.10E+04	1.50E+04	1.70E+04	9.10E+04
1-2 Hour After Removal	3.50E+05	8.50E+04	3.50E+04	1.00E+05
24 Hour Stabilization	2.60E+06	1.70E+05	6.80E+04	1.20E+05

Plasma Coating 2	Test points			
	1-2	2-3	3-4	4-5
Initial	1.00E+07	2.90E+04	4.10E+04	6.20E+06
1st Cycle	5.10E+06	2.10E+04	2.80E+04	1.90E+04
4th Cycle	4.70E+06	3.80E+04	3.70E+04	7.60E+04
7th Cycle	4.80E+06	4.50E+04	4.40E+04	9.10E+04
10th Cycle	7.60E+04	7.10E+04	6.00E+04	1.10E+05
1-2 Hour After Removal	1.80E+05	1.50E+05	1.20E+05	5.50E+05
24 Hour Stabilization	5.50E+06	3.90E+06	8.10E+04	1.90E+06

PC Specimen 1



PC Specimen 2



DWV Testing

- IPC-830-CC Specifies use of D Comb pattern for DWV testing

3.1 Qualification Testing, Classes 1-3 Five IPC-B-25A boards (see Figure 1) using the D comb pattern (one uncoated and four coated) with conformal coating according to the coating suppliers recommendations.

3.2 Conformance Testing Five IPC-B-25A Boards (See Figure 1) containing the C pattern ("Y" shape pattern) with 0.635 mm lines/0.635 mm spacing [25.00 mil lines/25.00 mil spacing] or minimum spacing on the production board, whichever is smaller, coated with conformal coating according to the coating supplier's recommendations.

- Mil-I-46058c uses C "Y" pattern

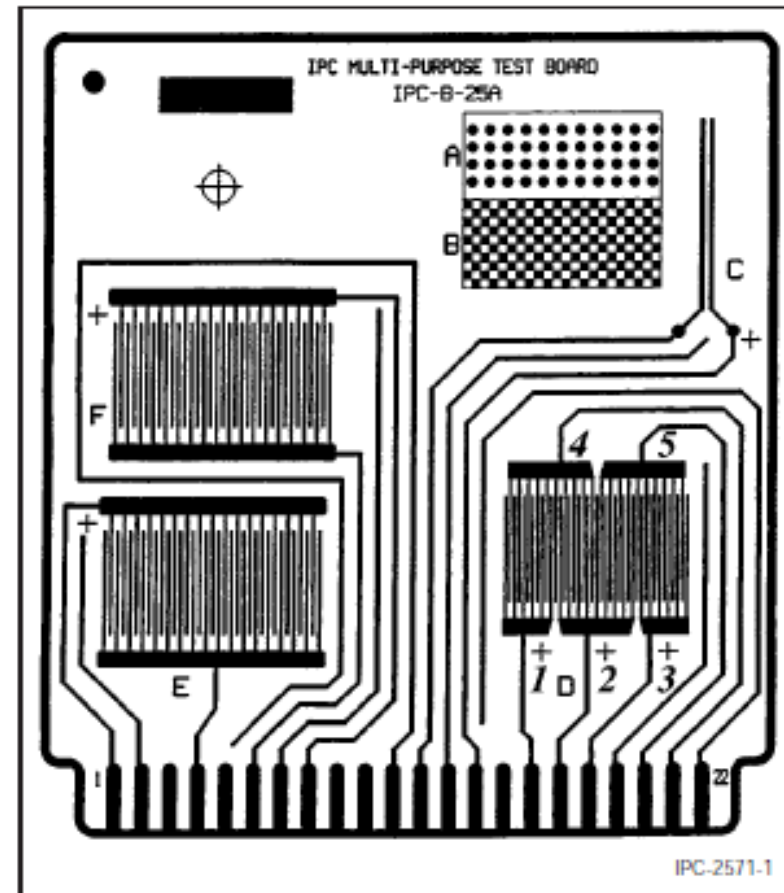


Figure 1 IPC-B-25A Test Board (Leads on D Pattern Are Identified)

DWV Testing

- As received:
 - 1 micron Plasma Coated B25a
- Moisture exposure, 20 cycles:
 - Temp: 20-65° C
 - Humidity: 83-95%
- Thermal Shock, 100 cycles:
 - Low temp: -65° C
 - High temp: 125° C

As Received		
	Voltage Achieved	
Sample	D Pattern	C Pattern
1	1500	1500
2	1400	1500
3	1380	1500
4	1380	1500
5	1360	1500
Moisture Exposure		
	Voltage Achieved	
Sample	D Pattern	C Pattern
1	1120	1500
2	1080	1500
3	1180	1500
4	1200	1500
5	1220	1500
Thermal Shock		
	Voltage Achieved	
Sample	D Pattern	C Pattern
1	1180	1500
2	1380	1500
3	1380	1500
4	1340	1500
5	1360	1500

Contact Resistance

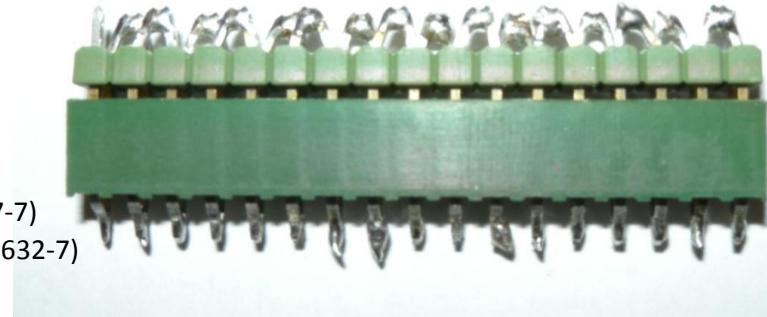
LLCR Measurements

Current (A) 0.01

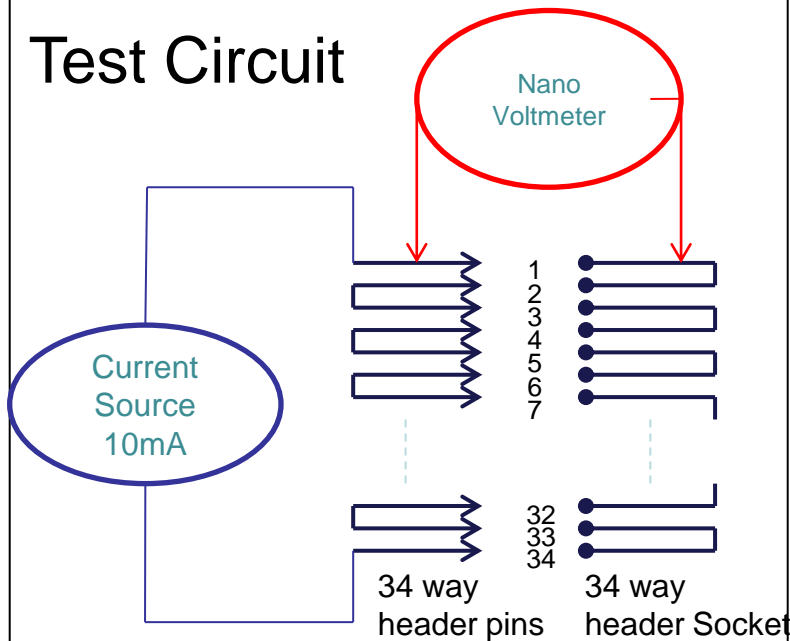
V comp (V) 0.1

Connector Male 34way Pin Header Au over nickel contact (TE Connectivity 1-215307-7)

Connector Female 34way Socket Header Au over nickel contact (TE Connectivity 1-826632-7)

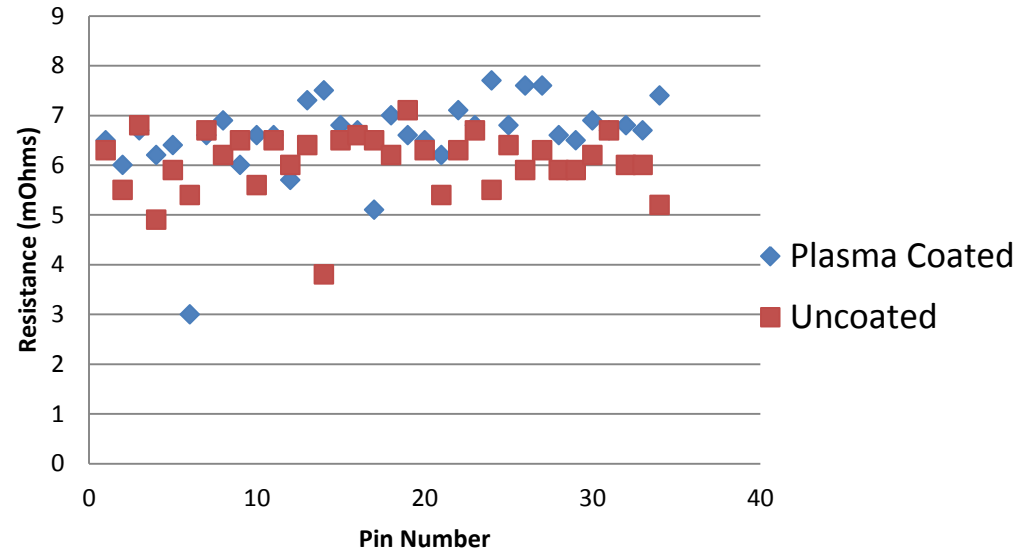


Test Circuit

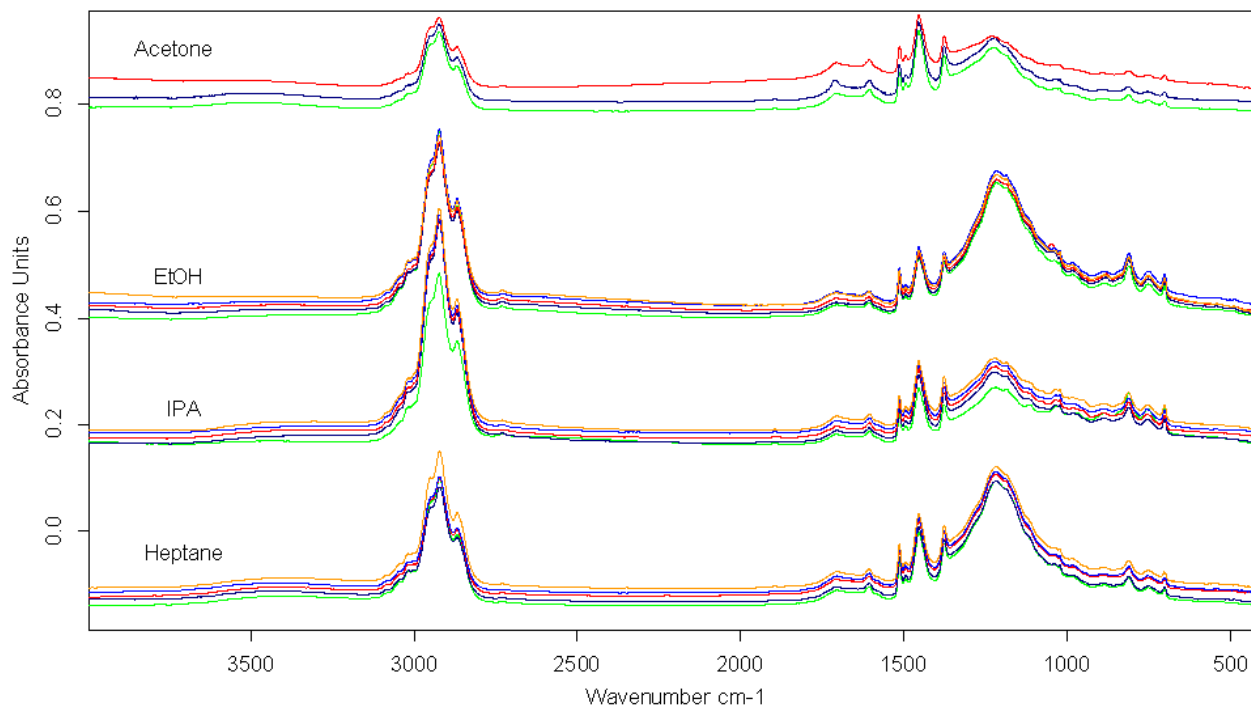


$$R_{\text{contact}} = V_{\text{measure}} / 10 \times 10^{-3}$$

Low Level Contact Resistance

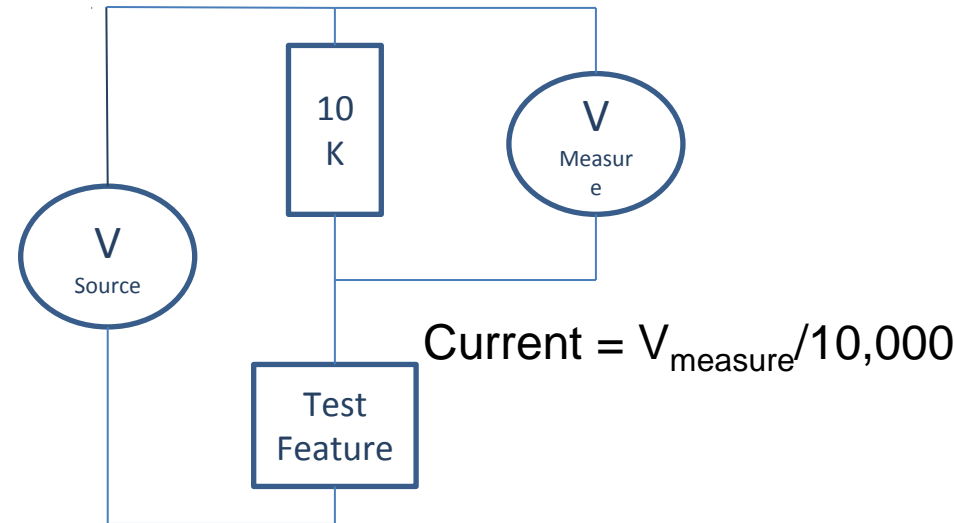
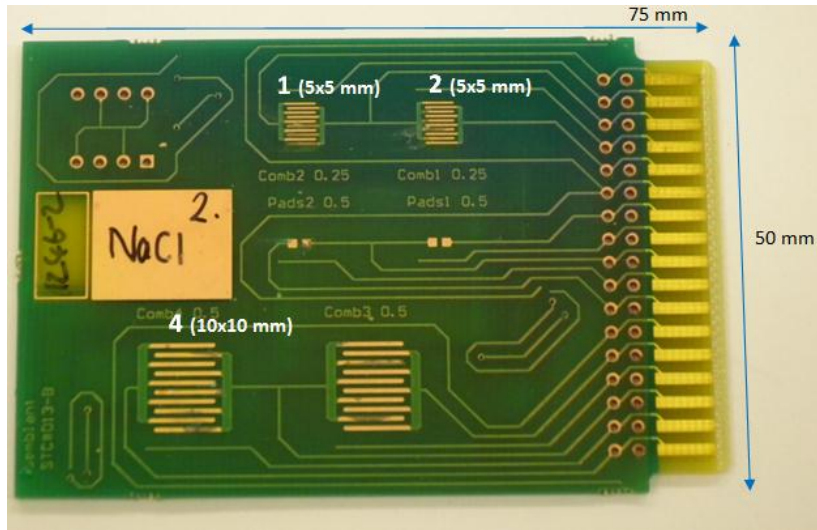


Chemical Resistance



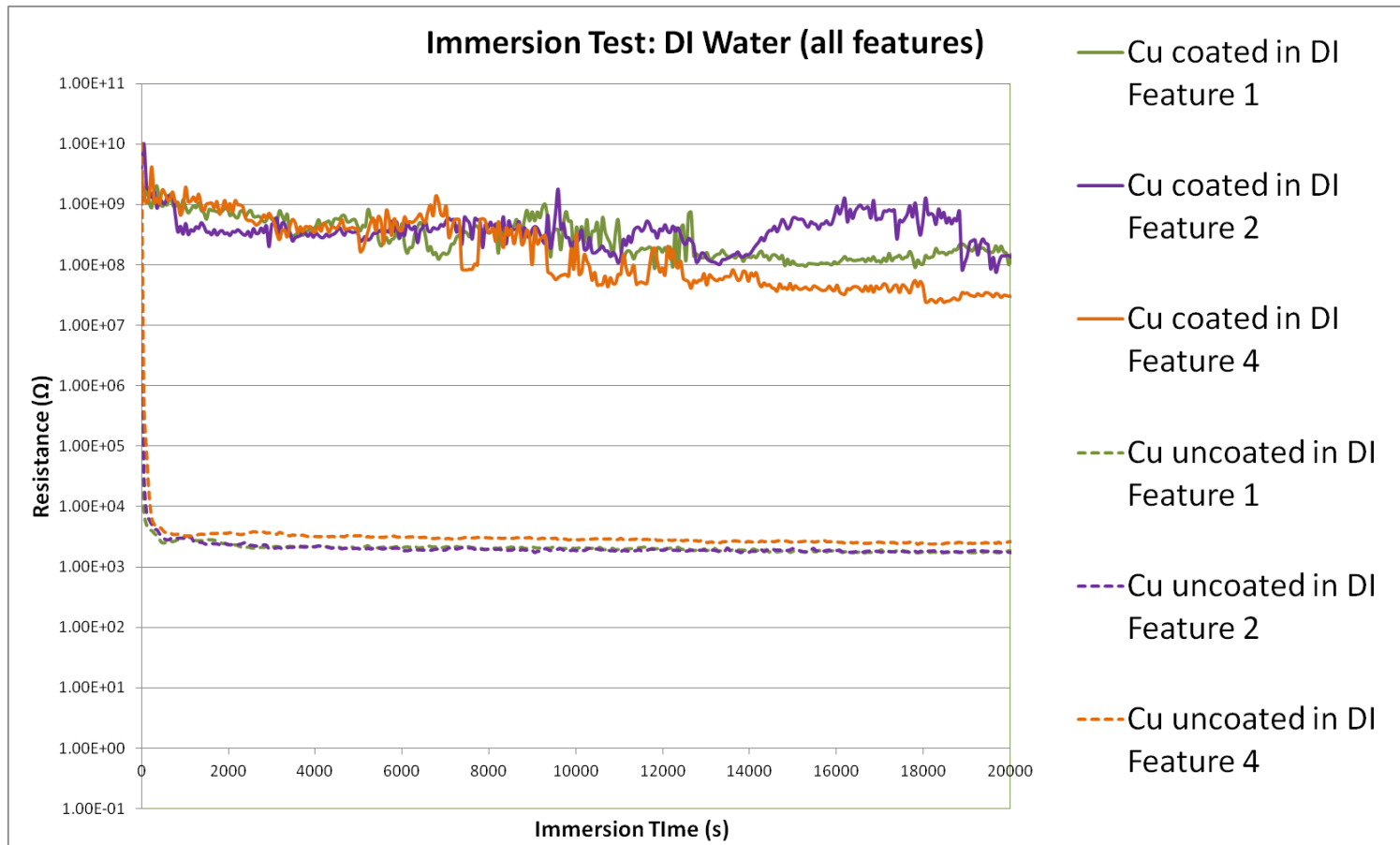
- FTIR spectra recorded before and after immersion in solvent for up to 24 hours
- Plasma polymer coatings exhibit excellent chemical resistance

Liquid Immersion Testing

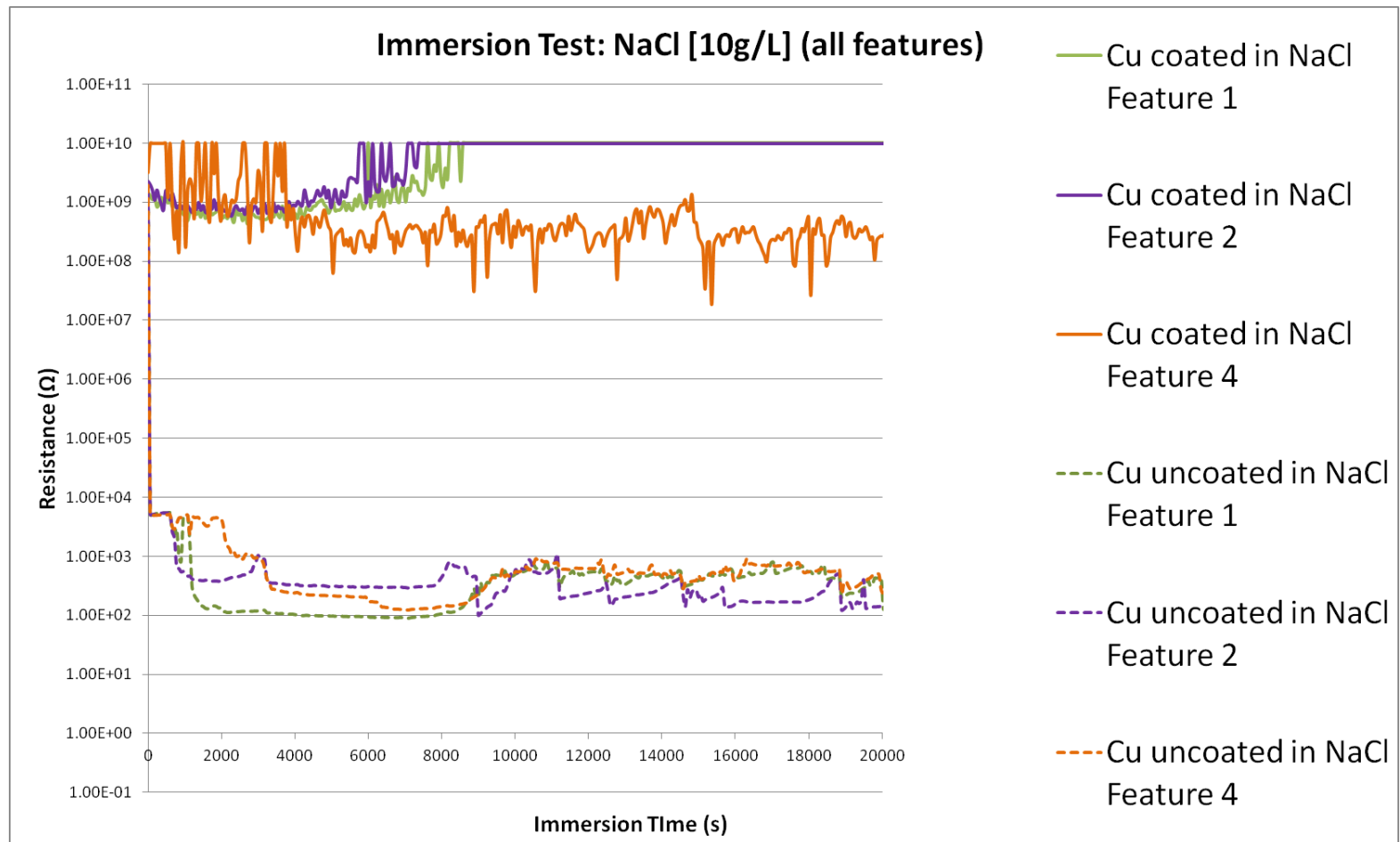


- Substrate: Bare Cu PCB
- Coating: 1 micron Plasma Polymer
- Applied Voltage: 5V
- Immersion Test Solutions: Distilled Water (DI) and NaCl (10g/L)
- Heat treatment conditions: 175° C for 30 minutes

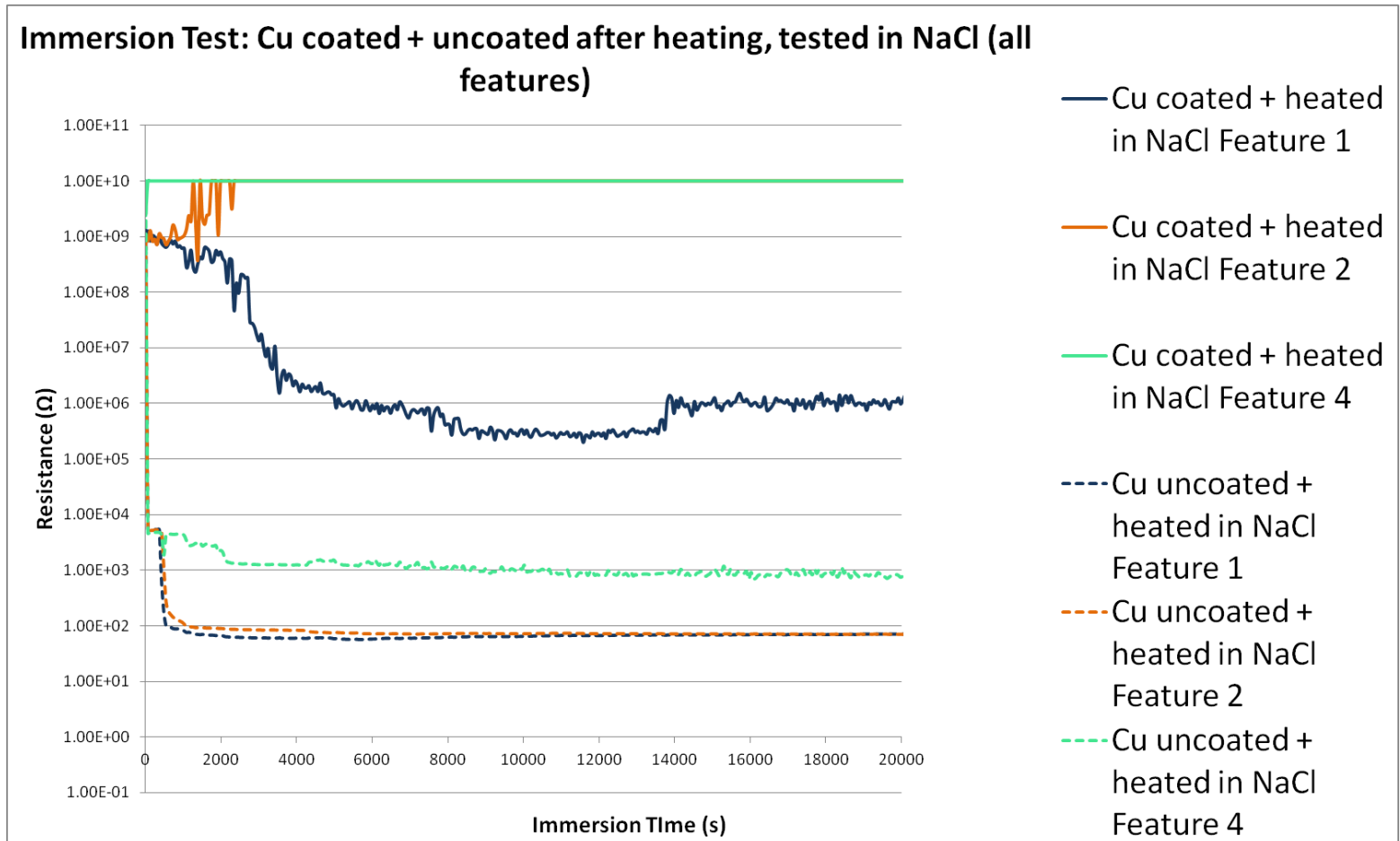
Liquid Immersion Testing



Liquid Immersion Testing



Liquid Immersion Testing



Liquid Immersion Demo



Conclusion

- Semblant uses plasma polymerization technique to provide unique coatings to protect electronics from harsh environment:
 - Plasma polymerization offers access to wide range of coating materials
 - Prevent corrosion and oxidation on various surfaces
 - Provides hydrophobic surface to repel water and other harmful liquids
 - Thin coating requires no masking of contacts
 - Makes rework of components simple

Future Work

- Continue work to qualify new class of materials under IPC830CC
- Continue coating characterizations
 - Thermal shock testing
 - Thermal / Physical properties
 - Chemical compatibility testing

Thank You!

Questions?