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Atmospheric Plasma Surface Engineering of Printed Circuit Boards: A Novel Method to Improve the Adhesion of Conformal Coatings

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Abstract
Conformal coatings are essential components for the microelectronics packaging industry. These functional coatings aim to protect electronic circuits from environmental factors such as heat and moisture. Typical coating formulations involve the use of epoxy, urethane and acrylic chemistries on polymer printed circuit boards (PCBs) leading to poor adhesion and failure to form void-free uniform coatings that follow the PCB skyline contour.

Plasma treatment is a novel method to increase the adhesion strength of the conformal protective coatings to PCBs through the removal of residual organic contaminants and surface activation. Poor adhesion can be a result of: i) incompatible materials, such as bonding polymers, ii) process residue: contaminants from fluxing, soldering and chemical treatments and iii) handling and storage conditions: fingerprints and dust. Plasma treatment under atmospheric pressure plasma (APP) conditions has emerged as an alternative solution for completely assembled PCBs which does not require a vacuum-based system. APP processes are fast and can be used for the treatment of selective areas of the board. The technology utilizes a dry gaseous medium and does not involve any harsh liquid solvent chemistries. Air-based APPs contain gaseous species that can react and remove organic surface contaminants very rapidly. Furthermore, they can be instrumental in the chemical functionalization and activation of the surface. In this paper, case studies from the application of air-based APPs for the cleaning of PCBs and the improved adhesion of conformal coatings will be presented.

Introduction
Historically, the vast majority of Printed Circuit Board Assembly (PCBA) conformal coatings were those used in high reliability mission critical material application areas such as automotive, aerospace, military, and medical products. Conformal coatings are applied on PCBs to protect the electronic components from environmental moisture, heat, handling, various contaminants and particulates. As the utilization of conformal coatings increases, the need to diagnose and prevent the root causes of coating defects such as contaminants becomes a critical component in electronics manufacturing. These surface residual contaminants may be either ionic or nonionic nature.

The main focus is the removal of ionic contamination since the majority of PCBA failure modes are ionically induced leading to corrosion and dendrite growth. Trace amounts are problematic as ionic contaminants encounter moist environments, charged species disassociate even in localized thin films and the conductivity of the solution increases. Understandably, high reliability standards and production practicality heavily emphasize ionic test methods as evidence of cleanliness in both qualification and production, but largely ignore non-ionic organics.

Non-ionic residues are non-conductive organic materials often introduced in the form of board fabrication materials, oils, resin, lotions, silicone, etc. While these contaminants can impact the operation and reliability of a PCBA (e.g. unwanted impedance), the greater concern is their negative impact on substrate surface energies resulting in poor adhesion and wetting issues commonly observed in solder mask, potting, underfill and conformal coating applications. Although a mature and well understood process, the conformal coating process does have common problems and challenges that manufacturers often face. Examples of four such common defects are shown in Figure 1.

Surface condition and preparation of the areas to be conformally coated is a key element to ensuring a successful and defect free process. Today, when it comes to high reliability PCBAs it is most common to clean / remove the flux via a de-fluxing process prior to conformally coating the assemblies. The industry relies on well-established criteria and measurement techniques for measure of a successful cleaning (de-fluxing) process. This includes visual and ionic cleanliness standards. PCBAs processed as such are considered by the industry to be "clean."

However, this standard of "clean" does not account for non-visible, non-ionic organic contaminates and thus very often a "clean" surface is not necessarily a bondable surface. Left on the surface, these contaminants can and do often result in the conformal coat defects that industry has struggled with for years.

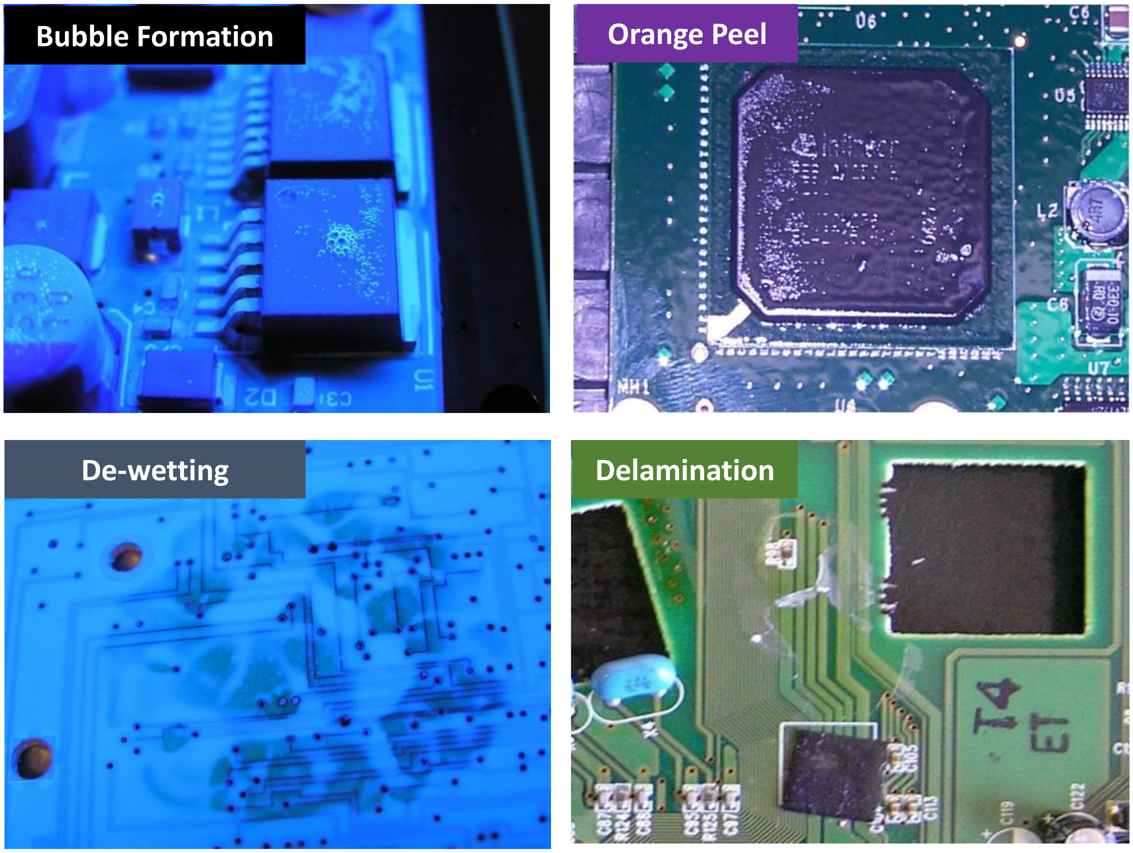

Figure 1 – Common Conformal Coating Challenges

Regardless of the formulation or application method, robust coating processes require coated surfaces to be clean, dry and surface activated to energy values greater than the surface tension of the coating material. Whether the surface energies are lowered due to undetected organic contaminants or substrate coating compatibility issues requiring the use of a primer, plasma leads to significant process improvement. Whereas vacuum based plasmas have been used for the cleaning and activation of polymeric materials for several decades [1], plasmas operating under atmospheric pressure conditions have been gaining a lot of traction due to the high throughput and the potential of becoming part of inline processing at manufacturing levels.

Materials and Methods

A plasma jet system which operates at atmospheric pressure is used for the pretreatment of the PCB materials. It is equipped with a kHz generator and a Plasma Control Unit (PCU), and so plasma parameters can be modified to optimize the process for the specific application, while critical plasma properties such as power and flow rate can be monitored at all times during processing. The plasma is generated by an arc discharge, which takes place upstream of the plasma jet nozzle, and a working gas (clean dry air, nitrogen, hydrogen). The working gas flow rates range from 40 - 75 lt/min. Upon exiting the nozzle, the plasma jet interacts with the substrate, and so the substrate is not directly exposed to the discharge zone but reacts with the neutral species that are produced in the plasma. Treatment width can range from 4 mm to 55 mm depending on the gap distance between the substrate and plasma jet and the nozzle-head component. The jet can be mounted on an automation robot enabling the user to control the gap distance which may range from 4 mm to 15 mm, and jet head speeds from 10 to 800 mm/sec.

Polymers are known to have low surface energy [2] that is typically manifested as water repellency. Figure 2 shows the contact of a small water drop on the surface of a hydrophobic (left) and hydrophilic surface (right). The measurement of the angle formed between the substrate and the drop outline provides information related to the properties of both the solid and the liquid and the interaction and repulsion of intermolecular forces between them. The balance between the cohesive forces of similar molecules (for example, hydrogen bonds and Van der Waals forces) and the adhesive forces between dissimilar molecules such as between the liquid and solid molecules (mechanical and electrostatic forces) will determine the solid/liquid interface contact angle.

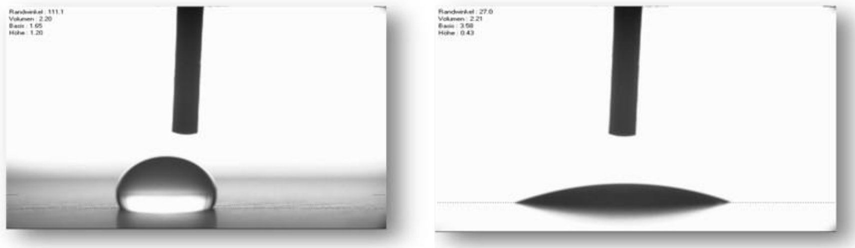

Figure 2 – Examples of surface energy and their associated water contact angles

In this work, the surface wettability was assessed using water contact angle (WCA) goniometry. The portable goniometer ballistically deposits a drop of water onto a surface. After the drop is deposited, the equipment algorithm uses a top-down view to take a highly precise image of the drop, in order to measure the contact angle.

Results and Discussion

As mentioned above, non-ionic organic contaminates very often remain on PCBAs even after de-fluxing, and when present these contaminants can result in conformal coating defects. Over the past decades, plasmas have shown that they can be highly effective at removing these contaminants. Figure 3 depicts the interaction of an atmospheric plasma jet with a polymeric substrate:

The impact of atmospheric pressure plasmas can be summarized as cleaning and functionalization of the exposed surfaces through the removal of surface residual impurities and grafting of new functional groups that improve the surface wettability. In air-based plasmas, the presence of nitrogen ions (N^+, $N2^+$), NO, N_2O, NO_2, NO_3, oxygen and nitrogen atoms, OH radicals and excited atomic and molecular species produce a very reactive phase. However, only the neutral charge species are allowed to react with the activated polymer surfaces. Therefore, plasma surface treatments lead to improved printability, dyeability, and increased surface energy. This is achieved through the functionalization of the surface mainly due to the presence of the above-mentioned oxygen-based free radicals generated in the plasma phase, which are grafted onto the surface during the plasma exposure. The plasma-induced surface modification does not cause any degradation of the bulk material properties since the treatment is surface specific and affects only the top 10 nm of the material [3]. The combination of cleaning and activation provided by plasma ensures that the PCBAs surfaces are well prepared for the conformal coating material.

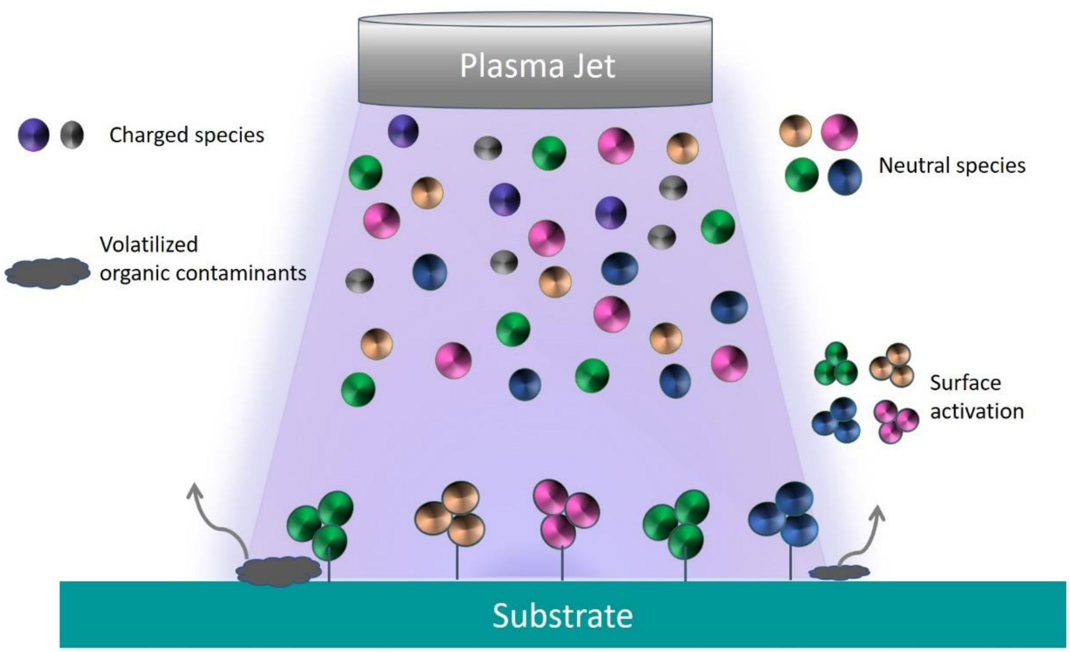

Figure 3 – Surface cleaning and activation

According to literature, plasma surface activation can enhance the adhesion between the PCB substrate and protective coatings. In a paper by Shin et al. [4], the interfacial adhesion between epoxy molding compound (EMC) and printed circuit boards were investigated. The adhesion energy increased with plasma treatment by over 50%, from 55 to 86 J/m^2. The improved adhesion was attributed to the increased density of polar surface groups due to plasma treatment, which helped enhanced chemical bonding between the EMC resin and the SR resin.

Case Study 1

Extensive de-wetting of PCBAs was observed after using traditional methods of surface cleaning. The PCBAs had been cleaned using a widely accepted de-fluxing process including an inline cleaning system and an aqueous based cleaning agent. The PCBAs were passing all visual and ionic contamination standard inspection methods. The theory was, that although they had a "clean" surface these non-visible, non-ionic organic contaminates remained on the surface, and that they were the root cause of the resulting conformal coating issues being experienced.

Water contact goniometry was used to assess the wettability level of the PCBAs prior to the conformal coating process. Table 1 below shows WCA data as measured at 5 different location points (solder mask, component bodies, solder pad). As shown, these PCBAs had an average WCA of 74.6° prior to the conformal coating process. A plasma process utilizing air as the plasma gas was applied to the PCBAs. Following plasma treatment, the average WCA dropped to 26.2°, which is an improvement of 65%. These results provided clear evidence of high surface energy prior to the conformal coating step, and that these contaminations were easily removed after the plasma application.

Table 1 – WCA (degrees) on a PCBA

Board Surface Preparation	**Board Location (Measurement Point)**					
	1	2	3	4	5	Average (°)
Before Plasma	87	68	77	75	66	74.6
After Plasma	25	30	30	22	24	26.2

Two subsequent tests were conducted: i) scratch and ii) pull tests. Both aimed to better understand the direct impact of the conformal coat bond strength and integrity. It is important to note, that as was the case with the PCBAs used for the contact angle testing, all PCBAs used for both the scratch and pull tests were first cleaned as per approved process: in-line de-fluxed using aqueous based de-fluxing agent. Measurement points again included solder mask, component body, and solder joint/pads for all three tests.

The scratch test as per Table 2 below shows ranking of conformal coat bond strength as a function of cohesive failure level. In this case, a rank of 10 represents full cohesive failure (best) and a rank of 2 represents adhesive failure (worst). The purpose of this test was to evaluate the impact of various surface preparation steps prior to conformal coat. As shown in Table 3 which lists the pull strength results, it is clear to see that the best results were achieved when plasma was used in the surface preparation process. It is also important to note that the worst result by far was when no added surface preparation step was used. Based on this test, plasma alone provided improvement over primer.

Table 2– Cohesive Failure (Scratch Test)

Surface Preparation Process	**Type of Cohesive Failure (10=Best, 2=Worst)**
Plasma	10
Plasma + Prime + Coat	10
Prime + Coat	8
Coat Only	2

Table 3 – Pull Strength

	Surface Preparation Process				Pull Test
Board	**Openair Plasma**	**Openair Plasma +Prime+ Coat**	**Prime + Coat**	**Coat Only**	**Average Force (lbs/ft)**
1	X				0.50
2	X				
3		X			0.54
4		X			
5			X		0.45
6			X		
7				X	0.23
8				X	

This series of tests make it clear that a "clean" surface is not always a bondable surface and that plasma as a surface preparation step is highly effective in the removal of non-ionic organic contaminates. Removal of these contaminants are critical to ensuring a successful conformal coating process. Additionally, in this case, the ability to eliminate the primer step could result in significant cost savings while improving the process. Lastly, although not a focus of these tests, coating uniformity was also improved.

It is worth noting that on average, PCBAs have a WCA range of 60° – 80° post de-fluxing ("clean" not bondable) and post plasma treatment the WCA is typically in the range of 20° to 30°.

Case Study 2

The focus of Case Study 2 was to understand the impact of plasma on uniformity coverage and thermal cycling. A total of five different UV curable conformal coating materials were used in this study. Conformal coating materials were applied by an automated dispensing system to ensure accurate and repeatable coating application. Plasma surface preparation was done using an atmospheric pressure rotational plasma jet. All materials were subjected to thermal shock testing. The temperature was cycled from -40ºC to 130ºC for 250 cycles while each cycle time was 30 minutes. An example of the atmospheric plasma treatment is shown in Figure 4.

Figure 4 – Plasma treatment of a PCBA

Three out of the four coatings tested showed better coverage through use of plasma treatment. Improvement was not observed with one of the coatings as this coating yielded a positive result under both conditions. An example of the coating coverage is shown in Figure 5.

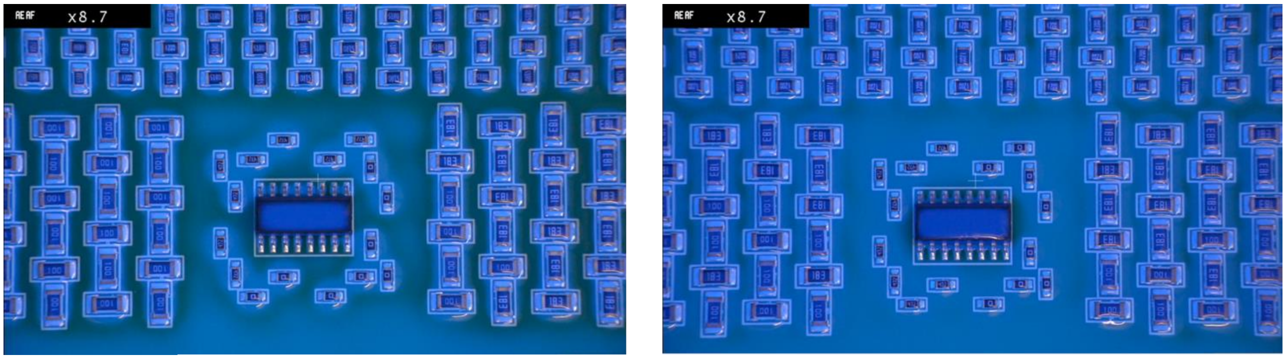

Figure 5 – Conformal coating coverage of untreated (left) vs treated PCBA (right)

Two out of the four coatings tested showed reduced delamination with plasma after thermal shock cycling tests. An example of delamination can be seen in Figure 6. Like above, improvement not observed with 2 of the coatings as they both performed well regardless of surface preparation.

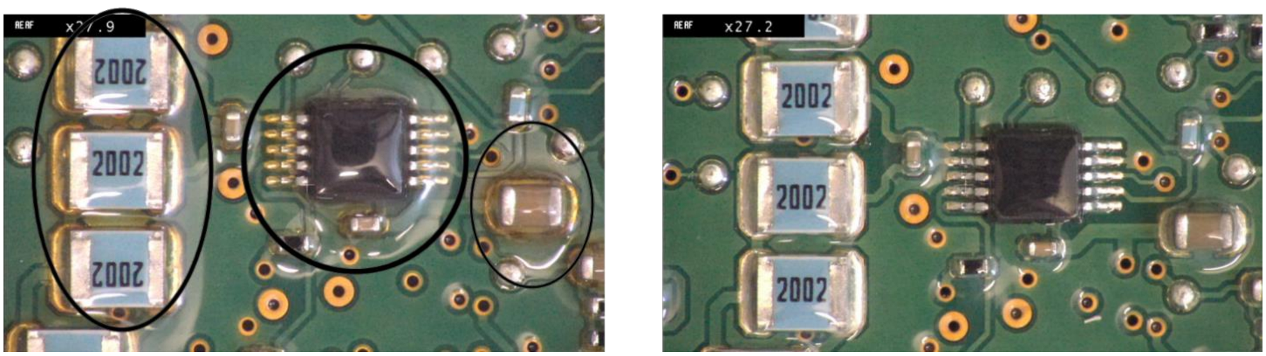

Figure 6 – Delamination on conformal coating on untreated (left) vs treated PCBA (right)

It is clear from this study that conformal coating material selection does play a role, but more importantly that surface preparation through use of plasma is critical. All tested samples that had first been treated via plasma had excellent coverage and uniformity and they held up to the exposed thermal cycle testing.

Conclusion / Summary:

Conformal coating on PCBAs has been a standard application for decades. However, manufacturers of electronic equipment face challenges like bubbles, orange peel, de-wetting, and delamination which are related to the cleanliness of the PCBA surface prior to the coating process. Atmospheric pressure plasmas can be effective in removing the surface contaminants. In Case Study 1, cleaning the PCBA surface with air-based plasma improved the average pull force, in pounds by 20%. Additionally, Case Study 2 showed, that plasma improved coverage resolution in three out of the four conformal coatings that were tested.

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