Humidity Robustness of Plasma-Coated PCBs

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Influence of Humidity, temperature and the bias voltage on the reliability of plasma coated PCBs

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Abstract

The reliability of Printed Circuit Boards (PCB) is at risk due to the continuous miniaturisation. As a result, PCBs are more susceptible to external factors such as humidity, temperature, contamination, etc., which affects the general performance leading to the failure of electronic devices. Therefore, Protecting the PCBs against these factors is gaining a great deal of importance. Plasma polymerisation process is used as a method to form a barrier by applying plasma polymer films on PCBs. The flexibility and simplicity of the plasma process make it an intriguing method for this purpose. However, the influence of humidity, temperature and the bias voltage on these samples is unknown. In this work, several methods are used to characterise two types of plasma coated PCBs (single layer and stacked coatings) as a function of humidity, temperature and a bias voltage. Electrochemical Impedance Spectroscopy (EIS) in combination with gravimetric moisture sorption technique are used to study the water uptake, while leakage current measurement is used to study the influence of an applied bias voltage between the electrodes of PCB samples exposed to a cyclic condition in the climate chamber. EIS and gravimetric techniques revealed minimal water uptake in the plasma coatings. Electrical DC testing resulted in the failure of single layer plasma coatings, whereas there were no changes observed in the stacked coatings.

1. Introduction
The continuous miniaturisation of Printed Circuit Boards (PCBs) increases their sensitivity to environmental factors. The miniaturisation leads to closer spacing on PCBs, and therefore enhancement of the strength of the electric field as this is inversely correlated to the distance. Moreover, in the presence of humidity and contamination, condensation can occur. Contaminations on a PCB can arise from the soldering process, degassing from the Printed Circuit Board Assemblies (PCBA) or the external environmental exposures [1], [2]. According to Matsumoto et al., the size of the dew droplet can range from 20-50 μm at around 50% Relative humidity (RH) [3], [4]. Thus, a corrosion cell can be easily formed even in the presence of low levels of humidity, contamination and an electric field. PCBs are often constructed from different materials. Presence of the thin electrolyte layer on a PCB can connect the various material, and therefore it can initiate the corrosion process [5]. An electrochemical process is often the primary reason for the failure of PCBs and eventually the failure of electronic devices. In particular, electrochemical migration is one of the main reasons for this failure. In the formed corrosion cell, oxidation on the anode results in the formation of the corrosion products. Due to the presence of the electric field, corrosion products migrate toward the cathode, and they grow further (dendritic growth) until the anode and cathode are bridged. This causes a short circuit and failure of the device [6]–[8].

Polymer films are still being used as a method to prevent corrosion of metals. On the other hand, plasma polymerisation process/plasma polymer films are receiving a great deal of interest [9], [10]. This method allows deposition of plasma polymer films on a wide range of materials. Moreover, the possibility of using different precursors enables the simple modification of the deposited layer, giving them unique properties. One of the significant advantages of this method is the ability to deposit thin conformal coatings in a one-step procedure, including the surface activation step and film-curing [11], [12]. Formation of plasma polymer films is strongly dependant on the degree of fragmentation of the organic precursor molecules in plasma, followed by their recombination and layer formation on the substrate. Hence, plasma polymer films own very different properties and characteristics in comparison to conventional polymer films. Despite the unique properties of these coatings, there are not many studies regarding their protection behaviour for PCBs. Some of the factors that cause and influence surface condensation are RH, the difference in temperature between the substrate and the surrounding environment, the presence of contaminations, porosity, etc. [8], [13], [14]. However, there is little knowledge regarding the influence of these factors on the reliability of plasma coated PCBs. In a number of works, the measure of the leakage current is used as a criterion for investigating the failure of PCBs. The magnitude of the leakage current is influenced by the severity and conductivity of the media [5]. Some researchers have investigated the failure of PCBs with different surface finishes by studying the leakage current and by using Electrochemical Impedance Spectroscopy (EIS) technique [2], [15], [16]. The presented work explores the influence of humidity build-up and temperature on the performance of plasma coated PCBs using the mentioned techniques. The possible impact of these parameters was evaluated by placing the PCB samples inside the climate chamber and measuring the impedance signal and the leakage current between the biased-voltage electrodes on the PCB. Furthermore, water/vapour absorption on the plasma
coated PCBs was studied with a gravimetric technique. Scanning Electron Microscopy (SEM) was used for sample imaging.

2. Materials and Methods

2.1. Materials
Blank PCB samples were provided by Elprinta NV (Belgium) with the copper tracks coated with Electroless Nickel/Immersion Gold (ENIG) as the final surface finish. Experiments were performed on the comb-pattern PCB sample (pitch size and distance =0.5 mm) as shown in Figure 1.a. A schematic of the cross-section of PCB samples is presented in Figure 1.b.

![Figure 1](image)

**Figure 1** a) comb-pattern PCB samples and b) schematic of the cross-section

Plasma coatings were applied on PCBs with an industrial plasma polymerisation reactor (Nanofics CD600 model, Europlasma NV, Belgium) with a capacitively coupled plasma source. The plasma polymerisation reactor has a rectangular shape made of aluminium with a volume of 0.282 m³. The walls of the reactor are grounded (see Figure 2).

![Figure 2](image)

**Figure 2** Schematic of the plasma polymerisation reactor

The reactor consists of 4 radio frequency powered electrodes (water-cooled) working at 13.56 MHz. Each RF-electrode is coupled with a grounded electrode with a 3 cm gap between the
two. The deposition process is performed at medium vacuum conditions to expand the plasma zone beyond the plasma generation zone. The medium vacuum conditions are obtained by using a roots compressor pump. The power range is between 10-1000 watts. Work pressure varies from 3 Pa to 20 Pa and the gas flow from 5-200 sccm. The temperature of the chamber is kept at 40 °C. Fluorinated acrylate monomers are used as precursors for the plasma polymer films with different thickness values on the PCBs; these fluorinated precursors are aimed at producing hydrophobic surface properties (the precursor is shown in Figure 3). PCB samples are placed on dedicated substrate fixtures which are outside the plasma generation zone (the zone between the RF and the grounded electrodes). Before introducing the inert gas or monomer vapour into the chamber, the system is pumped down to a base pressure (1.3 Pa). Upon introducing the monomers, the reactor reaches a predefined pressure, and then a plasma is ignited. At that time, the plasma activation (without precursor) or plasma polymerisation (when there is an injected precursor) initiates. The exposure time is different depending on the thickness of plasma polymer films. In the end, the remaining gas or vapour is flushed out of the system, and the system is aerated to reach atmospheric pressure.

![Figure 3 precursor (1H,1H,2H-perfluorodecyl acrylate) for plasma coating deposition](image)

Studied coatings in this work include two single layer coatings with the thickness of 1±0.15 μm and 9±1.35 μm and stacked coatings with the thickness of 1±0.15 μm and 3±0.45 μm. These coatings were applied to the samples after a activation pre-treatment of the substrate to increase the adhesion of the coating to the substrate. The process for deposition of stacked coatings contains a post-treatment on the single layer coatings before applying another layer on top. This process was repeated several times to achieve multi-layer stacked coatings on the substrate (full process conditions are proprietary information of Europlasma).

### 2.2. Gravimetric Moisture Sorption

The vapour sorption behaviour of the plasma coatings was studied using a “Proumid Vsorp” moisture sorption analyser. The experiments were performed at 25 °C and 85% RH. All the samples were placed on an aluminium crucible. For this experiment, silicon samples (10 mm x 15mm, thickness = 0.5 mm) were used as a substrate for the coatings. Before starting up the measurements, the samples were dried out in the instrument for 24 hours to be able to measure the weight of the samples at their dry stage. Then the RH was elevated to 85%. The changes in the weight of the samples were continuously measured for 187.4 hours.
2.3. Climate Chamber

Experiments were executed in an Espec PL-3KPH climate chamber. The fluctuation of temperature and humidity is ± 0.3 °C/ ± 2.5 RH%, in the range of -40 to +100 Degrees/20% RH to 98%RH. Experiments were performed at 93% RH and a changing temperature from 40 °C to 65 °C. The relative humidity during the test was kept at 93 %, while the temperature was cycled between 40 °C and 65 °C as illustrated in Figure 4. EIS and electrical DC measurements were performed in the climate chamber under this cyclic exposure condition. The cyclic condition stimulates the condensation on the surface of PCBs due to the temperature difference. Samples were placed in the chamber for 6 days. Electrochemical impedance spectroscopy measurements were performed for the first 3 days, and the rest of the days were dedicated to leakage current measurements.

![Figure 4 Cyclic temperature condition in the climate chamber](image)

2.4. Electrochemical Impedance Spectroscopy Measurements

The EIS measurements were performed in order to investigate the influence of condensation and water uptake in the coating. The tests were performed using a “Biologic VSP” multichannel potentiostat in the climate chamber with the same condition as mentioned in section 2.3. The signal amplitude of 25 mV was applied in the frequency range from 100 mHz to 100 KHz. Impedance measurements were generated at the open-circuit potential. The capacitance values were directly calculated from EC-Lab 11.21.

2.5. Leakage Current Measurement

Leakage current measurements were carried out on the samples in the climate chamber to evaluate the reliability of the plasma coated PCBs with humidity build-up. Therefore, the samples were exposed to 93% RH and a varying temperature as explained in section 2.3. The leakage current was measured as a function of time under a constant bias DC voltage of 10 V. 10 V is in the order of magnitude of the voltage present in an electronic device like a smart phone during operation.
2.6. Scanning Electron Microscopy

Field Emission Scanning Electron Microscopy was used for imaging, morphology and microstructural characterisation. A FE-SEM JEOL JSM-7100F was used for this purpose. The acceleration voltage and probe current used during the measurements were 15 kV and 30 pA, respectively. The working distance was 10 mm. Energy Dispersive X-ray Spectroscopy (EDX) connected to the FE-SEM was used for the elemental characterisation of the samples.

3. Results and Discussions

3.1. Water Sorption

Figure 5 shows the amount of water uptake in all different types of plasma coatings as a function of time. Each plot represents the mean of the values obtained from several measurements along with their standard deviations (shown with red bars). “dm” is the absorbed moisture content (gained weight) which is the difference between the weight of the sample at time t and the initial dry mass of the sample. Obtained results from the exposure of samples to 85% RH shows a minimal amount of water absorbed by the coating. However, this variation of the measured weight lies within the resolution of the instrument which is around 100 μg. When materials especially polymers are exposed to the environment with higher relative humidity, they exchange water/moisture until the concentration of the moisture in the coating is similar to the relative humidity of the exposed environment [17]. The ability of the material to absorb water is a function of its relative permittivity [18]. Therefore, the data indicates that these coatings have very low values of relative permittivity, and the negligible changes of the measured weight suggest that the relative permittivity does not change for any of the plasma coatings at this condition. In other words, the results represent the hydrophobic behaviour of the different types of plasma coatings under investigation.
3.2. Climate Chamber

3.2.1. Impedance Measurements

Results obtained by EIS measurements are presented in Figure 6. EIS was performed as a complementary technique to gravimetric water/ vapour sorption in order to study the interaction of water with a coating while condensation occurs due to cyclic conditions in the climate chamber. When a coating is pore/defect free, it acts as an ideal barrier which behaves as a pure capacitor [19]. In this case, the phase angle (θ) is almost 90°, and the slope of the impedance magnitude against frequency is about -1 [20]. Similar behaviour is observed for all the different types of plasma coatings in the present study, meaning that they act as a perfect barrier. Each impedance plot in Figure 6 consists of several impedance measurements at different times of the cyclic condition in the climate chamber (shown with different colours). The increase and decrease of the impedance signal with time are minor as it can be observed. Moreover, if electrolyte reaches the electrode or the metallic tracks on the PCB, then electrochemical reactions might happen at the electrode/electrolyte interface. These reactions are observed mostly as a plateau region at low frequencies in the impedance amplitude plots as shown in other works [2]. The absence of this low frequency response in the results supports the previous hypothesis that the plasma coatings on the PCB samples act as a barrier against external factors such as contamination or electrolyte. Additionally, the irregularities at low frequencies are due to the strong capacitive behaviour of these plasma coatings.
Figure 6 Bode amplitude (left) and phase (right) for a) 1 μm single layer b) 1 μm stacked c) 3 μm stacked d) 9 μm single layer plasma coated PCB samples

Figure 7 shows the comparison of all types of plasma coatings at their initial stage of formation of a thin electrolyte layer on the samples. The impedance magnitude of the 3 μm stacked plasma coating is slightly higher than all the other coatings. Higher impedance suggests higher resistance or higher protection behaviour in comparison to the other coatings.
Considering the relation between the impedance and capacitance (equation 1), higher values of impedance means lower values of capacitance.

\[ Z = \frac{1}{j\omega C} \quad (1) \]

Capacitance is correlated to thickness, surface area and the relative permittivity of the dielectric by equation 2:

\[ C = \varepsilon\varepsilon_0 \frac{A}{d} \quad (2) \]

C is the capacitance in Farad, \( \varepsilon_0 \) is the permittivity of the vacuum, \( \varepsilon \) is the relative permittivity of the material between the plates of the capacitor, A is the surface area (m\(^2\)) and d is the distance of the plates or in our case the thickness of the coatings (m). By comparing the 3 \( \mu \)m stacked and 9 \( \mu \)m single layer coating with eq. 1 and 2, it can be concluded that the relative permittivity of the 3 \( \mu \)m stacked coating is lower than the thick 9 \( \mu \)m single layer coating.

Furthermore, the changes of the impedance for each type of coating is related to the interaction of water with these coatings. To have a better insight of this interaction, the capacitance values were additionally measured at 79.121 kHz frequency, where the impedance data is dominated by the capacitive behaviour of the coatings. Changes of the capacitance as a function of time for each sample are plotted for all the samples in Figure 8.
The increase in the capacitance value is correlated to the water uptake when the temperature of the ambient in the climate chamber increases from 40 °C to 65 °C. The rise of the temperature in the climate chamber results in a temperature difference between the sample and the ambient leading to condensation and formation of an electrolyte film on the samples. Thus, the increase in the value of the capacitance is related to the water uptake in the coating, and the coating capacitance follows the cycling of the temperature resulting in a cyclic behaviour of the electrolyte condensation film formed on the sample surface. For a better distinction between the samples, the mean of the capacitance values at 40 °C, and the changes of the capacitance values due to water uptake are presented in Figure 9. It is confirmed here that the 3 μm stacked coating has the lowest capacitance and 1 μm single layer coating has the highest capacitance or the lowest impedance. However, the increase of the capacitance due to water uptake is minimal and almost similar for all the different coatings.
3.2.2. Leakage Current Measurement

The influence of an applied DC voltage and cyclic condition on the measured current as a function of time is shown in Figure 10. The small increase in the current profile (inset graph of Figure 10) is the result of humidity build-up and condensation on the coatings. The current level is less than 5 nA for all the samples. The presence of moisture in the environment can lead to the absorption of water molecular layers on the surface, and the thickness of this layer is dependent on the level of humidity. The combination of this water layer and a bias voltage can result in electrochemical migration and eventually an unwanted leakage current [21]. This leakage current is usually observed as a sudden increase (spikes) in the current profile. These spikes were only observed for the single layer plasma coatings. The failure rate and the time to failure of all samples are summarised in Table 1.

Figure 9 Capacitance of the plasma coated PCB samples at 40 °C and the increase of this value after water uptake as a result of exposure to cyclic conditions in the climate chamber.
Figure 10 Current response to a biased voltage of 10 V as a function of time of the plasma coated PCB samples

Table 1 Failure rate and time of failure of the plasma coated PCB samples

<table>
<thead>
<tr>
<th>Type of the coating</th>
<th>Failure rate</th>
<th>Time to failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 μm Single layer</td>
<td>75 %</td>
<td>2.64 ± 0.49</td>
</tr>
<tr>
<td>1 μm stacked</td>
<td>0 %</td>
<td>NA</td>
</tr>
<tr>
<td>3 μm stacked</td>
<td>0 %</td>
<td>NA</td>
</tr>
<tr>
<td>9 μm single layer</td>
<td>50 %</td>
<td>3.04 ± 0.06</td>
</tr>
</tbody>
</table>

The maximum values of the leakage currents for the 1 μm and 9 μm single layer plasma coatings are 254.18 nA and 22.84 nA respectively. It seems that the single layer plasma coated sample with the lowest thickness value was the most vulnerable to cycling condition and a biased voltage. According to the literature, the current level for dendrite formation and electrochemical migration is at milliampere levels [2]. However, the leakage current of the samples in this work is at nanometres scale. Therefore, Optical microscopy and SEM analysis were performed for a better comprehension of the possible reason for the failure of these coatings. No dendrite formation was observed on the samples by analysing them with an optical microscope (Figure 11). However, as can be seen in Figure 11.b, the 9 μm single layer plasma coated PCB sample has different features in comparison to the other samples. As-produced 9 μm single layer plasma coatings have a glue-like structure. This is possibly due to the inability of the plasma method to produce such thick films on the substrates. Therefore, after exposure to the cyclic condition in the climate chamber, these samples have a glossy appearance which is probably because of their glue-like structure and the absorption of the moisture on the coating. This characteristic can be seen at the reflective edges in Figure 11.b.
On the contrary, Figure 12 obtained with SEM shows the presence of cracks and irregularities on the surface of these samples. These images show clear differences between the single and stacked plasma coatings. According to other works [22]–[24], cycling conditions can lead to fatigue failure. Also, the different thermal coefficient of different materials can form stress and degrade the sample with each cycle. These damages to the coating could also be caused by the stress generated by the formation of corrosion products [25]. Elemental mapping with SEM-EDX on the 1 μm plasma coated PCB after the test is presented in Figure 13. Results show the presence of elements such as chlorine and calcium which indicates the possible contamination on the surface. Combination of these contaminations, condensation and a bias voltage resulted in corrosion and formation of corrosion products. Also, the stress originated from the corrosion products led to the crack propagation in the coatings. On the other hand, it was not possible to see these products on the 9 μm plasma coated PCBs.
Figure 12 SEM images of a) 1 μm single layer b) 9 μm single layer c) 1 μm stacked d) 3 μm stacked plasma coated PCB samples after exposure to the cyclic condition in the climate chamber and DC electrical testing.

Figure 13 EX mapping of 1 plasma coated PCB after the leakage current measurement a) SEM image b) Fluorine C) Carbon d) Oxygen e) Calcium f) Chlorine.
4. Discussion and conclusion

Our investigation highlighted the influence of humidity and temperature on the protection behaviour and water uptake of the different types of plasma coatings applied on the PCBs. Different methods were used for measuring the water uptake in the coatings such as electrochemical impedance spectroscopy, DC electrical testing and gravimetric moisture sorption. A clear difference between the different plasma coatings caused by the incorporation of moisture, temperature and applied voltage was observed.

By comparing the different coatings with gravimetric vapour sorption and the capacitance measurements, it was noted that all the plasma coatings absorbed a negligible amount of water. On the other hand, even though the 3 μm stacked plasma coated PCB showed higher impedance and lower capacitance, the changes of the capacitance after water uptake for all the coatings were minimal and similar. The minimal water uptake of the coatings is correlated to the hydrophobic properties of fluorine-based coatings.

On the other hand, the increase in temperature had a direct influence on the measured current as a result of DC electrical testing. These conditions led to the failure of the single layer coatings which appeared as a sudden increase of the measured current or leakage current. It was concluded that the sudden increase of current is due to crack propagation of the coating and not the electrochemical migration. The cracks are caused by thermal stress and the stress from the formation of the corrosion products.

As a general conclusion, the stacked plasma coated PCBs had a much better performance in comparison to the single layer plasma coated PCBs. Moreover, the results revealed the strong barrier properties of the stacked coatings against possible corrosion reactions on PCB samples.

5. Acknowledgement

6. References


