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# Surface Modification of a PCB Substrate for Better Adhesion of Inkjet Printed Circuit Structures

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## Abstract

The robustness and service life of inkjet printed electronic circuit structures are highly influenced by the state of the interface between these structures and the substrate. In the case of polymeric substrate materials, surface modification is necessary to realise a favourable interface, as these materials are generally not very receptive to chemical bond formation with the deposited ink. This paper deals with the surface modification of a high frequency laminate (substrate) using two different techniques to improve interfacial adhesion. The techniques deployed are $CF_4/O_2$ based plasma treatment and micro structuring using pulsed laser. The plasma treatment parameters were varied systematically using a statistical design of experiments. Substrates with varying surface characteristics, resulting from different plasma treatment parameters, were subjected to post-processing steps including surface energy and surface roughness measurements. Similarly, the influence of laser treatment parameters on surface characteristics of the substrate was also studied in detail. The outcomes of these two surface modification techniques are discussed in this paper.

***Keywords***: *Inkjet printing, Adhesion, Surface modification, Plasma etching, Laser ablation*

## 1. Background

Inkjet printing of functional inks is widely researched as a technique for electronics fabrication. However, being able to print the required circuit structures is a job half done if the robustness, reliability and lifetime expectancy are not taken into account. The response of a printed structure to mechanical, thermal and environmental stresses is a key aspect to be considered before deeming it suitable for practical applications. One of the most important factors that determine the robustness and reliability of a circuit structure is its adhesion to the substrate material. In general, adhesion of a thin film to a substrate depends on the affinity between the two materials, the mode and rate of deposition, the film thickness, the process temperature, the process pressure etc [1]. This holds true for inkjet printing as well, as a single layer of inkjet-deposited structures is typically less than a micron in thickness and hence can be classified as a thin film.

Within the framework of this research, inkjet printing is deployed as a technique to deposit seed layers for a subsequent electroless plating process, for the fabrication of conducting circuit structures, especially for high radio frequency (RF) applications. ***Figure 1 (below) presents the gist of this research and where inkjet printing fits in.***

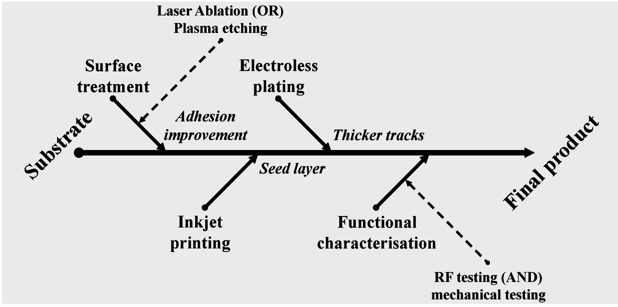
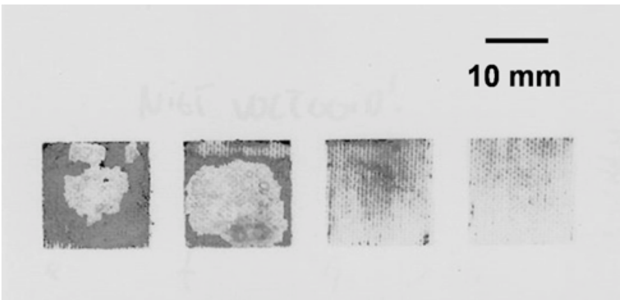



***Table 1 (below) shows the materials and equipments used for experiments relevant to this paper:***

| Type | Description |
|---|---|
| Substrate | Rogers RO4000 series high-frequency laminate |
| Ink | Harima Nanopaste (60% silver nanoparticles by weight) |
| Plating bath | Enthone Envision-2130 electroless copper system |
| Inkjet printer | Jetlab-4 drop-on-demand, piezo-actuated printer |
| Plasma etcher | TePla 3067-E barrel-type plasma etcher |
| Laser setup | Coherent Vitesse Duo with Coherent RegA regenerative amplifier |

Special RO4000 series substrates for inkjet printing (without copper cladding) were procured from Rogers Corporation, USA. The adhesion of inkjet printed silver structures on this substrate was insufficient, as indicated by scotch tape tests. It was also evident from the electroless plating trials, during which the silver seed layers delaminated from the substrate. ***Figure 2 (below) shows square-shaped silver seed layers inkjet printed on a RO4000 series substrate and subjected to copper plating; the delamination of silver due to poor adhesion can be clearly seen.***




To improve adhesion of the silver structures to the substrate, two different surface modification techniques were used: plasma etching and laser ablation. Plasma etching was investigated in greater detail using a statistical design of experiments (DoE). Conclusions concerning the substrate surface characteristics suitable for inkjet printing-electroless plating and the importance of surface modification for good adhesion were expected to be the outcomes of this research at the outset.

## 2. Plasma etching

**Introduction:** $CF_4/O_2$ plasma was chosen for this study based on prior experience and the available literature that extensively discusses the application of this gas combination to etch thermoset as well as thermoplastic polymers [2,3]. The chemical reactions are promoted by radicals in $O_2$ and $CF_4$. Within certain limits, the addition of $CF_4$ to an oxygen plasma greatly increases the etch rate. Even though oxygen is the etchant for polymers, atomic fluorine creates radicals at the surface of the polymer for further attack by oxygen [4]. The plasma treatment was intended to modify the wettability of the substrate surface and to impart sufficient surface roughness, so that mechanical interlocking is enhanced. However, very rough substrates or substrates with surface pores, as discussed in [5,6] were not intended, as they will have a detrimental effect on the accuracy of inkjet printing. In addition to that, roughened polymer surfaces have a deleterious effect on (RF-) electrical performance, especially in the case of high frequency circuits [7]. The DoE was used to identify the process parameter range which yields the most suitable substrate surface characteristics.

**Design of experiments:** The experimental design technique chosen for this study is the central composite rotatable design (CCRD). It gives sufficient information to describe majority of steady-state process responses and requires much fewer runs when compared to the full factorial design and gives a clearer picture about interactions between the process variables than a fractional factorial method. The CCRD was chosen in such a way that it contains '$2^n$' factorial treatment designs, '2n' axial or star points and sufficient replications at the centre of the design. Here, 'n' represents the number of process variables under study. Initial plasma etching trials showed that four factors, namely power, time of exposure to plasma, flow rate of $O_2$ and flow rate of $CF_4$ are most relevant parameters that need to be studied. The operating pressure, which is generally considered important in plasma etching, could not be pre-set in the available equipment. As a result, the CCRD consisted of 16 factorial treatment designs, with 8 star points and 7 centre points, thus 31 experiments in total. Power was varied from 2500 W to 4100 W in steps of 400 W, time was varied from 10 min to 50 min in steps of 10 min, $O_2$ flow rate from 0 ml/min to 2000 ml/min in steps of 500 ml/min and $CF_4$ flow rate from 0 ml/min to 200 ml/min in steps of 50 ml/min. A detailed explanation of the CCRD model is not presented in this paper; the model has been dealt with in detail in a separate paper [8].

Experiments and measurements: As per the experimental design, 31 substrates, each measuring 100 mm × 100 mm, were cut and subsequently plasma etched. In this etching process, the specimen i.e. substrate is immersed in plasma-containing gases that react with it. At a relatively high process pressure of more than 0.2 mbar, the mechanism for etching is predominantly chemical and the physical bombardment is minimal. The chosen gas flow rates were such that the process pressure was always above 0.2 mbar for all the experimental trials. The initial temperature of the plasma chamber was set as 80°C.

After etching, the contact angle of water on these substrates was measured with the purpose of calculating the surface energy of the latter, using the Neumann's equation of state [9]. The next step was the surface roughness measurement using a DEKTAK surface profiler, followed by analysis of the substrate surface topography using a scanning electron microscope (SEM). Subsequent to surface characterisation, rectangular test patterns with arbitrarily determined dimensions (30 mm × 10 mm) were inkjet printed on these substrates. The thickness of the pattern was highly dependant on surface roughness and surface energy of the individual substrates, and was difficult to characterise due to the pronounced roughness of certain substrates. Measurements on selected substrates after sintering of the test patterns indicated that the thicknesses were in the order of 1 $\mu$m. Scotch tape tests were done on these patterns to qualitatively rank the adhesive strength of the substrates under study. The spreading of the ink on the substrates was also studied to identify the optimal substrate surface characteristics.

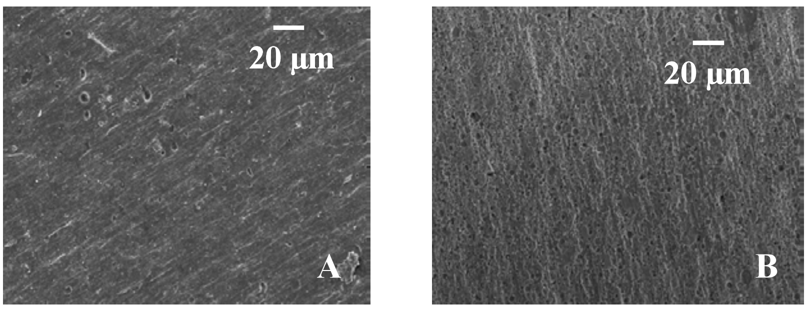
## 3. Laser ablation

**Introduction:** Plasma treatment etches the substrate as a whole, unless a mask is used to make the process selective. However, making a mask containing micro-patterns that allow the plasma to attack the substrate on specific locations is a time-consuming and expensive process. Hence, it was decided to use a laser ablation setup that directly etches desired patterns on the substrate i.e. it enables selective patterning of the substrate. The advantage of selective patterning is that if different inks have to be used on the same substrate to inkjet print different functional components, the size and shape of the patterns can be locally varied depending on the flow properties of the ink. The setup used in this study is a femto-second laser with a wavelength of 800 nm and a pulse length of 250 fs. Due to the extremely short pulse duration and small beam size, the material is ablated locally, resulting in minimal substrate damage due to the reduced heat-affected zone [10].

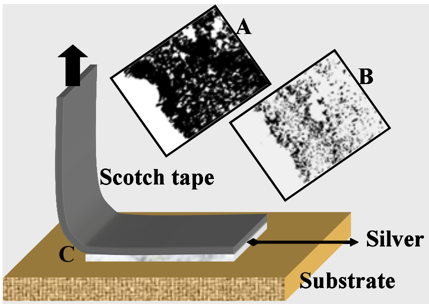
**Experiments and measurements:** The output power was maintained at 1 W. The focal spot size was varied between 5 and 20 $\mu$m, the pulse repetition rate was varied between 10 and 250 kHz, and the scanning speed, from 20 to 200 mm/s. Two different patterns were ablated: hatches and holes. The patterned substrates resulting from the various parameter combinations were analysed using a SEM and subsequently, silver structures were inkjet printed on selected substrates. Finally, scotch tape tests were done to qualitatively check for adhesion.

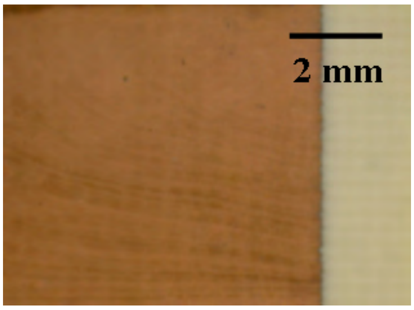
## 4. Results and discussion

The plasma treatment yielded substrates with varying surface roughnesses and surface energies, depending on the parameter set used. Based on surface roughness and surface energy measurements, as well as adhesion tests and droplet spreading observations, a substrate that was etched at 3300 W for 10 minutes, with $O_2$ and $CF_4$ flow rates maintained at 1000 ml/min and 100 ml/min respectively, was selected as the one with optimal surface characteristics. ***Figure 3 (below) depicts RO4000 series substrate (A) before plasma etching and (B) after plasma etching with the optimal parameter set.***



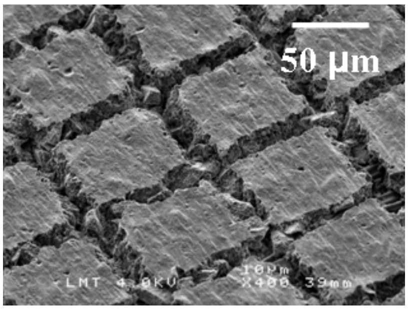

The selected substrate had a Ra value of 0.56 $\mu$m and a surface energy of 47.2 mN/m. The scotch tape test indicated an improvement in adhesion. It was also possible to electroless plate copper on silver seed layers printed on this substrate. ***Figure 4 (below, left) depicts a schematic of the scotch tape test method; it also shows pictures of two scotch tapes peeled off from silver structures printed on RO4000 series substrate (A) before plasma treatment and (B) after plasma treatment. Figure 5 (below, right) shows a plasma treated substrate on which silver seed layer was inkjet printed and copper was plated subsequently.***

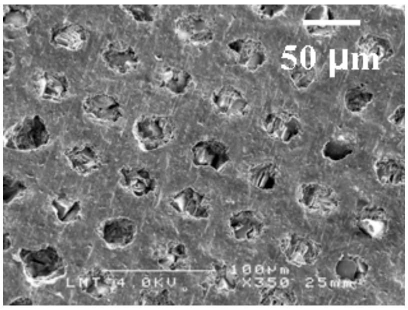



It is evident from the figure 4 that only minimal amount of silver was peeled off from the plasma etched substrate. That too, the failure was not adhesive but cohesive. This indicates that the adhesion between silver and the plasma treated substrate is higher than the cohesive strength of silver. The increase in adhesion can be attributed to the greater mechanical interlocking due to the increase in surface roughness of the substrate, and to the change in functional groups on the surface of the polymeric substrate.

Finding the correct laser ablation parameters proved to be difficult due to the composite nature of the substrate. The substrate is comprised of 3 materials: polymer matrix, glass fibre reinforcements and ceramic fillers. The laser beam penetrated the polymer top layer and encountered the other two materials; the parameters optimised to ablate the polymer did not hold good for the other materials. SEM analysis of ablated substrates showed that the laser-generated patterns were as much as 10 $\mu$m deep, much more than the intended depth of 1 to 3 $\mu$m. The problem with deeper patterns is they can lead to local agglomeration of functional ink particles during printing, resulting in huge variations in the cross-section of printed structures. This will affect both the electronic functionality and mechanical properties of these structures. ***Figure 6 (below, left) depicts a substrate with laser ablated hatched patterns and figure 7 (below, right), a substrate with laser ablated holes.***




Experimental investigations are currently going on to ascertain the right process parameters to obtain the desired depth of ablated profiles. To keep the local agglomeration of functional ink particles to a minimum, only the pattern showed in figure 7 is subjected to further optimisation. Laser ablated holes of 1 to 3 $\mu$m depth and 15 to 20 $\mu$m diameter are expected to be the outcome of the optimisation trials.

## 5. Conclusions

- Inkjet printed structures on plasma treated substrates showed improved adhesion.
- Increase in surface energy and surface roughness are responsible for improved adhesion.
- This enabled electroless copper plating on silver seed layers without adhesive failure.
- Laser ablated patterns were too deep (~10 $\mu$m), leading to local agglomeration of the ink.
- This affects mechanical as well as (RF-) electrical properties of the printed structures.
- Optimisation of the dimensions of laser ablated patterns is currently done.

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