Electroless Plating on Plastic Induced by Selective Laser Activation

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This paper presents a new method for the selective micro-metallization of polymers. A Nd:YAG laser was employed to draw patterns on polymer surfaces that were submerged in a liquid (usually water). After subsequent activation with palladium chloride and followed by auto-catalytic electroless plating, copper deposited only on the laser tracks. The mechanism of the palladium activation step was analyzed based on experimental results and theoretical calculations. It is believed that the laser introduces porous, rough structures on the surface, which favor palladium attachment. Looking from the surface property point of view, the basic polymer surface tends to attract palladium in an acidic solution. Using the laser treatment, standard grades of thermoplastic materials such as ABS, SAN, PE, PC and others have been successfully metallized. The metallized tracks are as small as 300 µm in width with 50 µm between two tracks, but further optimization is expected in future work. Due to the porous, rough structure of the laser track, excellent adhesion between the metallized layer and the substrate is obtained. On top of the first copper layer, additional metals such as nickel, gold, palladium or tin can be deposited.

Keywords: *Plating on plastic, laser activation, pattern plating.*

Introduction

Molded interconnect devices (MIDs) can be defined as thermoplastic components with electrical infrastructure (conductive tracks) or electrical components. MIDs are manufactured using a large variety of processes, but what is common to all process chains is the use of injection molding. Conventional injection molding, two-component injection molding and insert molding have all been reported[1] for this use. Another commonly used process for MID manufacturing is laser direct structuring (LDS). LDS involves the use of special polymers (filled with an organometallic complex or similar) and a laser structuring process, followed by electroless plating in the laser treated areas.

Laser induced selective activation (LISA) is a new technique that can do positional selective metallization of a polymer surface. As illustrated in Figure 1, there are three primary steps included in the LISA process:

1. The polymer surface is modified by laser in a medium of deionized water
2. The laser modified specimen is activated by submerging it in a palladium solution and
3. The activated specimen is plated using autocatalytic electroless plating.[2]

The main difference between the LISA process and LDS is that the polymer employed in LDS needs to contain a special filler, such as an organometallic complex or an inorganic spinel compound. The laser beam will induce a physicochemical reaction with the filler and the resulting released metal atoms will act as the catalytic nuclei for electroless plating. This process, however, is expensive, since the entire polymer has to be filled with special particles, while only the filler in the surface is used. Moreover, only relatively few polymer grades suitable for LDS are commercially available.[3,4]

In an alternative process, the entire surface may be metallized first, and then, in later steps, the unwanted metal areas are removed, for example by laser ablation or photolithography, followed by etching, but these methods usually involve either toxic chemicals in the pre-treatment, such as chromic acid, or sputtering, and often lead to a substantial waste of metal since most of the metal layers are removed.[5] Table 1 makes a comparison between LISA and other techniques.

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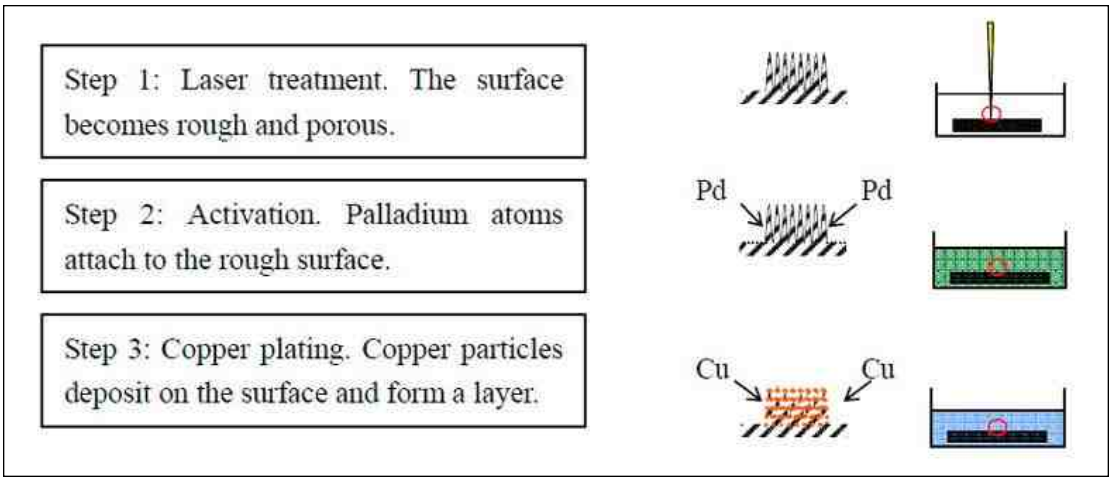

Figure 1—*Schematic illustration of the main LISA steps.*

Mechanism hypothesis

The substrate materials were injection molded polymers, such as polycarbonate (PC) or polystyrene (PS). Black grades were preferred in the study for their good absorption of laser beam energy, but other colors can be used as well.

The work piece was machined by a laser in a medium of deionized water. Deionized water is easy to obtain, safe and inexpensive, and reduces the possibility of unknown reactions. Other types of liquids may also be used in the future and may lead to different results.

In the laser machining step, the polymer surface will absorb the laser pulse energy in such a way that a thin layer on the surface melts. It is then instantly cooled down by the water surrounding it, so the polymer solidifies quickly and maintains a molten-like structure. After several passes (15 - 30 passes) of the laser, the surface will be full of peaks and pores, due to the random distribution of the pulses. The roughness, or the surface structure of the track, is determined by the laser energy input.

During the activation step, the porous structure will retain some activation solution in the holes, in which palladium atoms attach to the surface. Then, when the sample is submerged in the copper bath, the copper solution will make contact with the palladium attached to the surface, causing copper to deposit on the palladium sites. After that, more copper will deposit and propagate to form a continuous layer. Also, copper particles are entangled with the surface material, creating a strong mechanical adhesion between the copper layer and the polymer surface. Lastly, one has to consider that if the standing peaks from the laser treatment are too high, it will take a long time for the copper layer to reach and cover the top. Therefore it is necessary to regulate the laser parameters such that the laser track's roughness and height are optimized in relation to both the adhesion force and plating time.

Experimental set-up

A lamp-pumped Q-switch Nd:YAG laser (wavelength 1064 μm) was employed in the process. The laser beam traverses in a wobbly way, which increases the machined area. The beam velocity optimized for LISA was 60 mm/sec and at the optimized setting, the average output power was around 3.4 W.

The second step is the palladium (Pd) activation. Before activation, the laser tracks must be completely wetted by water. A fresh mixture of $PdCl_2$ and $SnCl_2$ solution was used as the activator bath, in which the following chemical reaction takes place:[6]

$$Pd^{+2} + Sn^{+2} \rightarrow Pd^{0} + Sn^{+4} \quad (1)$$

During this step, reduced palladium atoms adhere to the laser-modified surface, and become the active sites for copper growth in the subsequent electroless plating step. The process takes five minutes at room temperature, and the work pieces must be rinsed carefully with distilled water after this step.

Table 1
Comparison of LISA with other techniques

	LDS	MIPTEC[5]	Full-metallization	LISA
Materials	Special filler in materials and only a few materials are available	Thermoplastic and ceramics	Thermoplastic	Common thermoplastic polymer
Laser	Special wavelength to crack the bonds, special laser head to shape the track	Special wavelength to remove the metal layer	Special laser wavelength to remove the metal layer	The laser energy can be absorbed by the materials
Wet step	Electroless plating	Electroplating and metal etching after sputtering	Dangerous chemicals for the pre-treatment	Activation and electroless plating

The final step is the autocatalytic electroless copper plating, according to the reaction:[6]

$$Cu^{+2} + 2H_2CO + 4OH^- \rightarrow Cu^0 + H_2\,(g) + 2H_2O + 2HCOO^- \quad (2)$$

No external power supply is needed, as electroless copper deposits on the activated sites of the surface. It takes one hour to obtain approximately a 5-μm (200-μ-in.) thick copper layer. To prevent corrosion and oxidation and to be applicable for industrial use, a thin layer of nickel and gold can be deposited on top of the copper layer.

To decrease the plating time, a reactivation method was tried. After several minutes in the copper bath, the work pieces were taken out and re-activated in the same activation bath for five additional minutes, and then returned to the copper bath. In the reactivation, palladium deposits on the plated copper, so the activated area is increased. Since copper grows faster on palladium than on itself, it was felt that the plating time could be shortened.

To explore the copper deposition process, some tracks were only plated for a very short time, indeed too short for complete coverage of the copper, such that copper had just started to deposit on palladium atoms. Both the surface and cross-sectional views of those tracks were observed by scanning electron microscopy (SEM).

Results

After the laser treatment, the surface became spongy and porous, as shown in Fig. 2.

The surface wetting character was obviously changed, as illustrated by the advancing contact angles measured by a Dataphysics® OCA Series contact angle system and related SCA software. The laser-modified surface became much more hydrophobic than the original surface. The advancing contact angle of distilled water increased from 86°, on the original surface, to 146° on the laser-modified area, as shown in Fig. 3. Therefore, if the laser tracks are completely dry before the activation, it becomes very hard to wet them again, and palladium has no means of entry to attach to the surface.

Experiments showed that a completely dry sample needed at least two hours in the activation solution to achieve the same plating result compared to a sample that was not allowed to dry after the laser machining. Therefore, it is highly desirable that the laser tracks be wet before the activation. The easiest method to keep the surface wet is to simply store the species in water right after they are machined by the laser. One may also submerge the work pieces for 24 hours prior to activation and plating.

After the activation, it is desirable that any activator solution outside the laser track be removed, because it can lead to metallization with weak adhesion, and large area metallization may cause spontaneous plating bath decomposition.

The reactivation method mentioned earlier was found to increase the deposition speed quite effectively. If the plating was stopped after 2.0 min, and the surface was reactivated for 5.0 min, after another 43 min of plating, the copper layer was as thick as 4.8 μm (188.9 μ-in.), on average. Without reactivation, the thickness was only 2.0 μm (78 μ-in.) in 45 min.

On the basis of this work, the recommended plating procedure was:

1. Wet the surface. Submerge the work pieces in water for 24 hr or in alcohol solution (>50%) for several minutes, if the laser track is dry.

2. Wash the surface by spraying with alcohol, then by spraying with water, and finally submerging in water for one minute.

3. Activate for five minutes.

4. Cascade rinse carefully in distilled water.

5. Electroless copper plate for one hour or more, depending on the desired copper thickness.

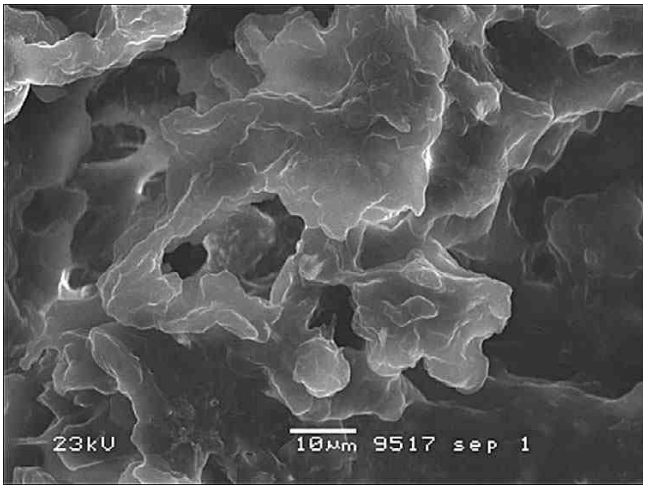

Figure 2—*Spongy structure formed after the laser treatment on polyethylene (PE).*

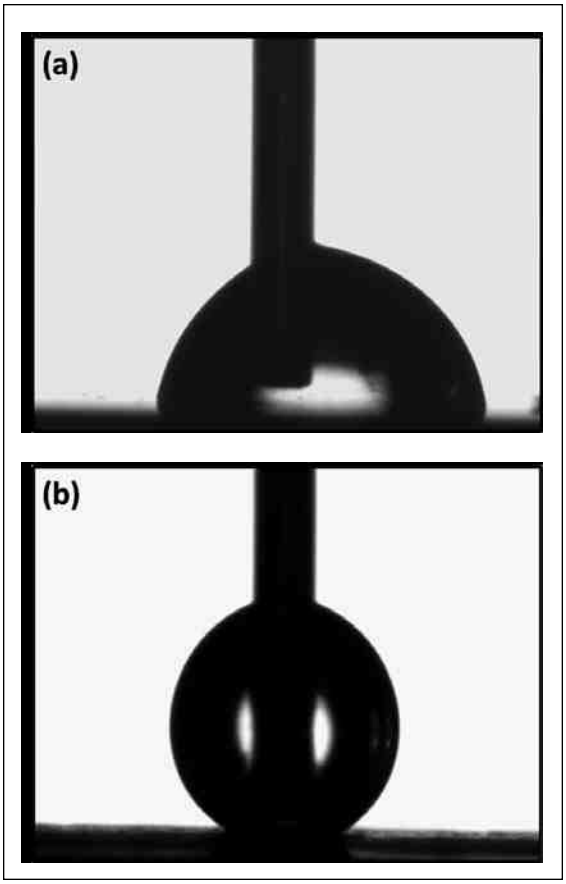

Figure 3—*Contact angle measurement on (a) a normal PC surface and (b) a surface treated by the laser.*

To illustrate how the copper propagated during plating, laser tracks plated for 1, 2 and 3 minutes on both polyethylene and polycarbonate were observed by backscatter imaging, using a scanning electron microscope (SEM), as shown in Fig. 4 (polyethylene) and Fig. 5 (polycarbonate). The bright dots in the pictures are heavy elements, *i.e.*, copper particles, in this case.

The cross-sections of the polyethylene samples have a clear layered structure after laser treatment. Figure 4a shows that after 1.0 min, copper starts to deposit in the middle layers. In Fig. 4b, copper propagates along the top layer and in the third minute, copper continues to grow along the top surface, while also starting to deposit at other sites in the middle layers, as depicted in Fig. 4c.

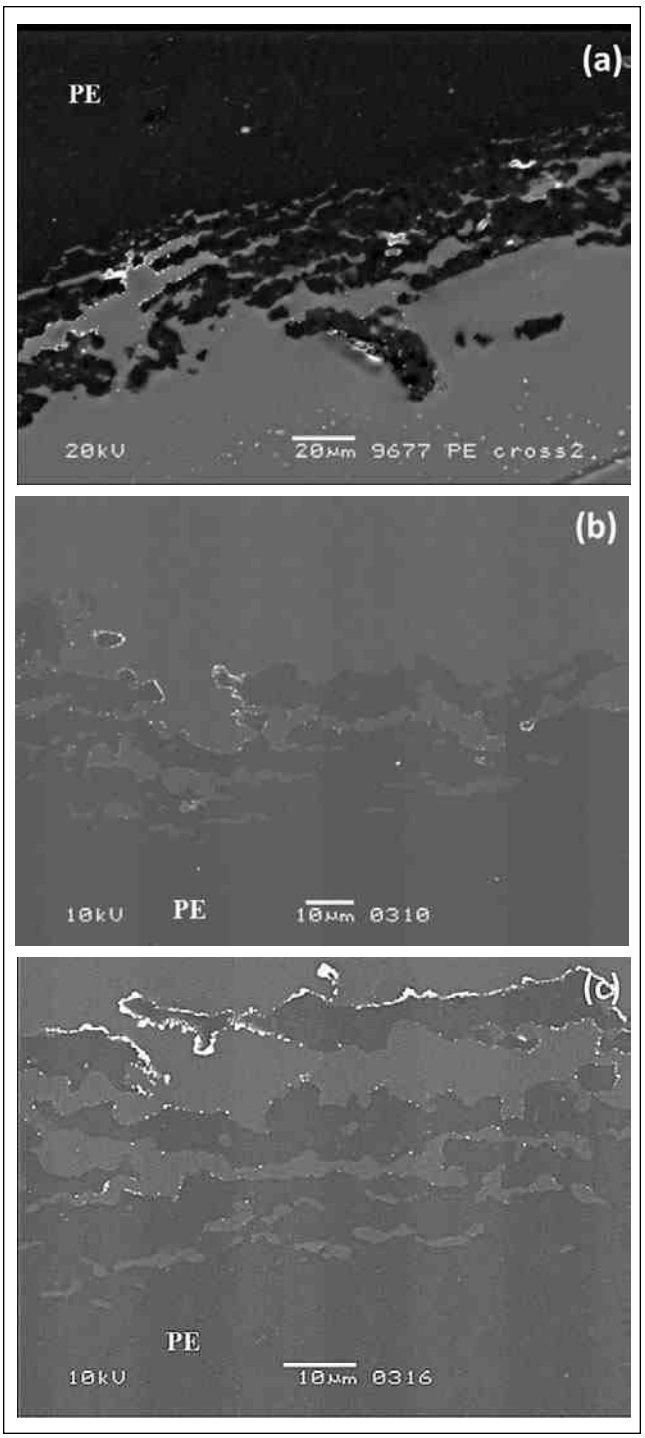

Figure 4—*Cross-section of polyethylene (PE) plated for (a) 1.0 min, (b) 2.0 min and (c) 3.0 min.*

In the polycarbonate sections, the layered structure is not as obvious, but the deposition trend can be clearly seen. Copper also grows preferentially along the top surface, since it is clear that more bright dots are seen in Fig. 5b (3.0-min deposit) than what is seen in Fig. 5a (2.0-min deposit). Figure 6 shows the surface view of a polycarbonate sample plated for two minutes. It can be seen that copper starts to deposit in a hole, but not generally on the surface.

As a qualitative examination for adhesion strength, a tape test was administered and passed with no problem. Adhesion was measured quantitatively with a DFD® hydraulic tensile adhesion tester (PAT model GM01/6.3 kN Adhesion Tester). The adhesive strength of the copper layer averaged 2.79 MPa for a polycarbonate substrate when the copper layer was 5.0 μm (196.9 μ-in.) thick.

Conclusion

This paper introduces a new selective metallization method for polymers. In this method, less toxic chemicals are used when compared to other techniques such as laser ablation or a 2k injection molding MID process. The electroless copper plating bath employed is a commercial product, and is easy to obtain. The low-power laser used is also standard. As a whole, the LISA process is cost efficient and environmentally friendly. A wide range of thermoplastic as well as standard laser equipment can be used to practice this technique, and it has been demonstrated that the copper layer has a good adhesion to the substrate. Work on exploring the mechanism behind the process is in our future plans.

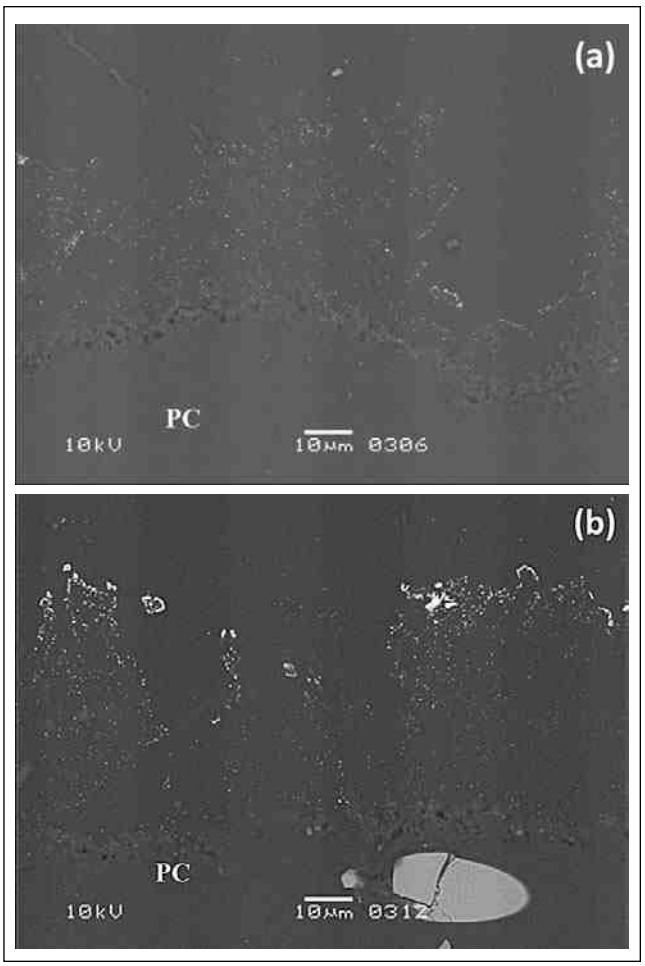

Figure 5—*Cross-section of polycarbonate (PC) plated for (a) 2.0 min and (b) 3.0 min.*

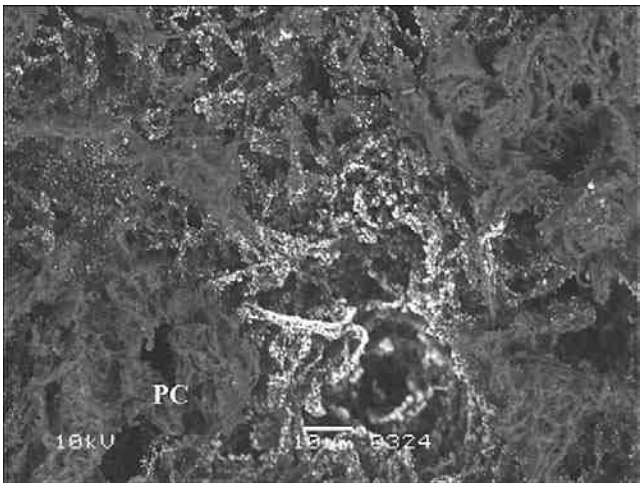

Figure 6—*Surface view of polycarbonate (PC) plated for 2.0 min.*

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Professor Hans Nørgaard Hansen is working in the field of Micro/Nano-manufacturing. He deals with establishing the basis of industrial production of products and components in metals, polymers and ceramics in the micro- and nanometer regime. Specific activities include product development, materials development and development of processes and production systems focused on micro-mechanical systems. The core activities comprise micro-product design and development, tooling technologies for micro-injection molding and micro-metal forming, mass production technologies, chemical and electrochemical processes and laser technologies. Finally the integration of processes into coherent process chains is a key activity.

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