Reel-to-reel patterned plasma activation of polymers at atmospheric pressure for the cost-efficient production of flexible printed circuits

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Abstract: Results of the work to develop a new potentially cost-efficient reel-to-reel technology for the production of flexible printed circuits (FPC) based on patterned atmospheric pressure plasma treatment, here also referred to as plasma printing, and subsequent electroless plating are presented in this contribution. For instance, copper metallized structures with widths and spaces down to 100 µm on polyimide and polypropylene were produced.

Keywords: ambient pressure plasma, microplasma, plasma printing, flexible printed circuit

1. Introduction

A key step in the successful electroless plating of polymers is the formation of a catalyst seed layer on their surface. Among the commonly applied catalysts in electroless plating is palladium (Pd) metal deposited in finely divided form on the polymer [1]. A suitable plasma treatment of polymers may lead to significantly increased Pd coverage and to adherent metallizations on the substrate [2, 3]. In earlier studies carried out in our group Pd coverage on polyimide films was found to increase by a factor of 10 – 20 when the substrates were activated in a dielectric barrier discharge (DBD) with forming gas mixtures at atmospheric pressure prior to Pd seeding based on ionogenic Pd solutions. This effect is attributed to the presence of additional nitrogen-containing functional groups such as amino groups on the polymer surface to which Pd²⁺ ions can bond via the lone electron pair at the nitrogen.

Peel strengths according to DIN 53494 of copper metallizations on polyimide reached 1.4 N/mm [4]. Such values are sufficient for applications in electronics. With a suitable equipment ambient pressure plasma activation of polymers for electroless metallization can be carried out area-selectively in the so-called plasma printing process [5].

In this article, we publish for the first time results of reel-to-reel plasma printing experiments. These experiments were carried out within a joint project with partners from industry and academia to develop a cost-efficient technology for the manufacture of flexible printed circuits (FPC).

2. Experimental

Copper(II) sulphate pentahydrate (min. 99 %, Merck), aqueous formic aldehyde solution (Rotipuran, 37 %, Carl Roth), aqueous hydrochloric acid solution (37 %, Fluka), palladium(II) chloride (Applichem), potassium sodium tartrate tetrahydrate (min. 99 %, Merck), sodium hydroxide (min. 97 %, Merck) and sodium hypophosphate monohydrate (min. 99 %, Merck) were used as purchased. Purities of the gases used were 99,999 % (helium, Air Liquide), 99,999 % (nitrogen, Air Liquide) and 99,999 % (argon, Air liquide) The forming gas mixture purchased (90 vol. % nitrogen of purity 99,996 % + 10 vol. % hydrogen of purity 99.9 %, Linde) was diluted with inert gas to a hydrogen content of below 4 vol. % before use in order not to exceed the upper explosion limit in air. Polymer films of polyimide (Kapton 200 HN, 50 µm thick, DuPont) and biaxially oriented polypropylene (Goodfellow, 50 µm thick) were used as purchased. In this paper these polymers are also referred to as respectively PI and BOPP.

Main components of the experimental plasma printing set-up included a high voltage (HV) electrode and a printer roller similar to those known from rotogravure printing as counter electrode. The HV electrode system had a curved shape with a curvature corresponding to the radius of the printer roller. Main components of the HV electrode system included a curved plastic carrier plate covered with an elastic polymer foam layer on the concave side to which a polymer film gold coated on the particular side facing the foam was attached. The gold coated area determined the effective electrode area which was usually 16 x 8 cm in this work. The printer roller used was a copper galvanized steel cylinder with a chromium top coat with the structures to be plasma printed engraved by means of ‘XtremeEngraving’, an electromechanical
engraving technique [6]. A gas shower positioned close to the HV electrode supplied the process gas. During operation the printer roller rotated and the polymer film was pulled through the gap between the electrodes for plasma activation.

![Fig. 1 Principle of reel-to-reel plasma printing](image)

Pressure of the HV electrode on the substrate was adjusted such as to allow a reasonable process speed on the one hand and on the other hand to ensure formation of process gas-filled spaces and ignition of a plasma in these spaces in positions such that the structures on the printer roller were accurately reproduced on the substrate. The ideal situation is shown schematically in Fig 1. Here plasma ignition occurs exclusively inside the ditches and depressions of the structures engraved on the printer roller during face-to-face contact between the printer roller surface and the polymer foil. Line-and-space widths of the structures on the printer rollers used in this work varied between mm and µm dimensions, the minimum structure width being 50 µm. Depth of the structures varied between 15 and 35 µm. With structures of such small dimensions microplasmas are formed. Typical operation parameters included sinusoidal mid-frequency (15 kHz) voltages estimated to be in the range of 10 – 20 kV, a gas flow of up to 70 slm and speeds of 0.5 m/min up to 1 m/min. A picture of the equipment used to carry out reel-to-reel plasma printing experiments is shown in Fig. 2.

Metallization of the plasma printed structures was carried out using galvanic processes conventionally applied in the metallization of plastics. In the first step a palladium catalyst layer was formed on the substrates by consecutive immersion for typically 5 min in an acidic 3 mmol/l PdCl₂ solution at room temperature and thereafter for 5 min in an 0.1 mol/l aqueous sodium hypophosphate solution kept at a temperature of ca. 50 °C. Electroless copper plating was then carried out using a non-commercial bath containing 0.2 mol/l copper(II) sulphate, 0.175 mol/l sodium hydroxide, 0.1 mol/l potassium sodium tartrate and 0.16 mol/l formaldehyde with a deposition time of ca. 5 min at room temperature. After each of the aforementioned process steps of the electroless metallization procedure the substrates were thoroughly rinsed with deionised water. Layer thickness of the copper deposit as estimated based on electron probe microanalysis (EPMA) data was ca. 30 nm. Galvanic reinforcement of these deposits was performed using commercial copper plating baths (Enthone Cuprostar 1525 and Cuprostar LP-1) at room temperature. Top coatings were applied to protect the copper surface from oxidation and were based on silver (Enthone AlphaStar) and an organic surface preservation (Enthone Entek plus HT). Adhesion of the metallized structures on the polymer was determined using a pull strength test according to the DIN standard EN 482, however, in variation with the DIN standard with thicknesses of the metal deposits after their galvanic reinforcement of only 3 – 5 µm. Soldering tests were carried out using high melting lead-free solders based on tin-silver-copper alloys. Shear strengths of solder joints were determined according to the standard MIL-STD-883E.

XPS measurements to determine the Pd surface concentration were carried out with the PHI 5500 Multiprobe technique spectrometer using a non-monochromatic MgKα radiation (hν = 1253.6 eV), with the emission voltage of 14 kV and emission current of 20 mA. A pressure of approximately 8·10⁻⁹ mbar was utilized in the analysis chamber. The electron take-off angle was 45°. Wide- and high-resolution spectra were taken at 187 and 23 eV pass energy, respectively. The peak deconvolution was done with the MultiPak Software V5.0A from Physical Electronics.

3. Results and discussion
In this work reel-to-reel plasma printing with area-selective surface functionalization of polymers aimed to be suitable to obtain adherent metallizations in subsequent electroless and galvanic plating processes was investi-
gated. Plasma process gases were therefore chosen to introduce selectively amino groups into the polymer surface and included pure nitrogen, forming gas (97 vol. % N₂, 3 vol. % H₂), mixtures of forming gas/helium (70 vol. % He, 27 vol. % N₂, 3 vol. % H₂), forming gas/argon (70 vol. % Ar, 27 vol. % N₂, 3 vol. % H₂) and nitrogen/helium (70 vol. % He and 30 vol. % N₂).

XPS measurements on polyimide films after palladium seeding (Fig. 3) show a significantly increased palladium concentration on the plasma treated polymer surface compared with the non-plasma treated reference [5]. The greatest increase in Pd coverage could be achieved using the forming gas/helium or the nitrogen/helium gas mixture. Significantly less Pd was found, however, on the polymer surface when forming gas was diluted in argon instead of helium. Apart from the process gas composition reel-to-reel speed seems to be a factor relevantly influencing the Pd coverage. In experiments using the forming gas/helium mixture an increase of the reel-to-reel speed from 0.5 m/min to 2 m/min led to a decrease of the Pd coverage of nearly 50 %. A possible explanation for this effect would be a lower degree of surface amination at higher speed (i.e. shorter treatment time), however, further investigation is necessary to confirm this hypothesis. For samples treated in forming gas/helium the standard palladium seeding procedure was varied in that the immersion time of 5 min in the palladium chloride bath was reduced to 1 min and 10 s respectively. The same Pd surface concentration was obtained regardless whether the sample was immersed for 10 s or for 1 min. An immersion time of 5 min yielded only ca. 20 % more Pd on the polymer surface. According to the evidence from the deconvolution of the Pd peaks in the XPS fine scan spectra Pd was generally present in the form of Pd⁰ indicating reduction with hypophosphite was incomplete. This result is of importance for further process optimization work since only Pd⁰ catalyses the electroless reaction [7].

Metallization results correlated with the Pd coverage of the polymer. Best metallizability and reproducibility of the metallization results were achieved using plasma activation with forming gas/helium or nitrogen/helium. In the experiments performed so far the absence of helium or its replacement by argon led to less complete metallization of the plasma printed structures. The beneficial effect of helium may be explained by a shift of the discharge characteristics from more filamentary towards more glow discharge-like with a resulting more homogeneous and more complete functionalization of the substrate surface.

An example of a copper metallized structure with line-and-space widths ranging from mm down to 50 µm on polypropylene as carrier material is shown in Fig. 4.

Results of the pull strength tests performed with copper structures coated with an oxidation protection coating based on silver (Ag) or on an organic surface protection (OSP) are shown in Fig. 5. In the case of PI the average
value for the pull strength reached 9.5 N/mm². This is already near the region of values generally considered acceptable by the FPC manufacturers for thermoplastic/thermosetting materials (≥ 10 N/mm²). Pull strength in the case of BOPP reached only ca. 4 N/mm². Such values may, however, still be sufficient for some selected applications.

Apart from the metal-polymer adhesion there are other parameters or properties of importance for the qualification of FPC for electronics production. Among these is the processability along the typical process steps in electronics production, a key criterion being the behaviour of the metal-polymer complex during soldering. Flexible circuit boards produced in this work such as the one of which a part is shown in Fig. 4 with PI as carrier material were subjected to soldering tests. Good wetting of the solder on the metallization and good solderability was observed regardless of the type of oxidation protection (Ag or OSP) applied. Furthermore no delamination of the metallization from the polymer was observed. Shear strengths of the solder joints reached values similar to those obtained with conventionally produced FR-4 circuit boards. No soldering tests were conducted with boards with BOPP as carrier due to too low thermal stability of this material.

The range of materials investigated more closely with respect to their suitability for reel-to-reel plasma printing has recently been extended to poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), polyether imide (PEI) and polyetheretherketone (PEEK). These materials are possible lower cost replacements for PI.

4. Summary and outlook

Atmospheric pressure reel-to-reel plasma printing with area-selective surface modification of polymer film surfaces suitable for subsequent electroless metallization and galvanic reinforcement was successfully demonstrated for substrates including PI and BOPP and copper as metal. Best metallizability of the polymers was achieved after their plasma activation in forming gas/helium or in nitrogen/helium. Via this technology produced polyimide-based flexible circuit boards with copper metallized structures with line-and-space widths down to 100 μm were subjected to solderability testing. Good wetting of the solder on the metallization as well as good solderability was observed. Shear strengths of the solder joints reached values measured with conventionally produced FR-4 circuit boards. With PI as carrier material average pull strengths of copper metallizations of 9.5 N/mm² were obtained, a value being already very close to the region of values generally considered acceptable by FPC manufacturers (≥ 10 N/mm²). Metallizations on BOPP were considerably less adherent with maximum values for the pull strength of ca. 4 N/mm².

Future work will be directed to a major part towards the improvement of the reel-to-reel plasma printing process, in particular with respect to cost, quality of the structure reproduction on the substrate and reproducibility of the results. Other focusses will be on the improvement of the metal-polymer adhesion and on a further reduction of the structure dimensions. A mature reel-to-reel plasma printing technology is of key importance in a concept for a cost-efficient continuous FPC manufacture based on a production line comprising the complete process chain from patterned plasma activation over electroless and galvanic plating to assembly and interconnection.

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