New methods for selective metallization of 3-D polymer microparts

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Abstract

The development of microdevices would be well served by integration of electronic connects into 3-D packaging. A number of technologies have been proposed in which conductive paths are created on polymer structures, e.g. by local activation of organometallic components present in plastic. But these suffer either from limited 3-D freedom, yield problems in mass production or excessive use of chemicals. Here two new and patented methods, selective etching and selective masking, for selective metallization for the production of three dimensional integrated devices are presented, which do not use precatalyzed polymers. After initial tests, a two-shot moulded three-dimensional test object with solder patches, through holes and varying track widths was used to test their selectivity and reproducibility for selected polymer combinations. The selective etching method gave for the PA4.6-PET combination excellent results with regard to the selective plating and subsequent reflow soldering. The second method, selective masking could be applied to a LCP-PPS combination, however process stability needs to be improved.

Keywords: metallization, integrated electronics, two-shot moulding

1. Introduction

Moulded Interconnect Devices (MID) is a generic term for technologies in which conductive paths and moulded polymer parts are integrated into one component. MID technologies give new opportunities for miniaturization of complex devices, e.g. antennae in a cell phone. Integration of functionalities into one component reduces assembly costs and product volume.

The core of MID technology is the ability to realize (insulated) conductive paths on or in a polymer moulded structure [1]. A number of approaches are used, some of which are suitable for 3-D geometries. These include (i) insert moulding with metal foil structures, (ii) physical or chemical vapor deposition with masks, (iii) (UV-)light induced metal deposition on the bottom of channels or cavities filled with a metal compound solution [2] and (iv) electroless plating of a surface that is locally perceptive for metallization [3]. The first is complicated because of the manufacturing and vulnerability of the foil structures, the second suffers from shadow effects and complicated mask design for 3-D projections. The third method requires a transparent flat substrate and is basically 2-D. The last method is the most important technique in practice.

Two variations are used: two-shot moulding with a precatalysed and non-precatalysed polymer and local activation by laser of a plastic with an organometallic component. In the first method, a two-shot moulded component is made out of a pre-catalysed and a non-precatalysed polymer. Because the former contains metal catalysts (nuclei) it can be metallized by an electroless plating process. The latter cannot and hence selective metallization of the surface results.

A number of dedicated precatalysed polymer granulates have been introduced on the market, e.g. a LCP (liquid crystal polymer) by Ticona and a PCB (printed circuit board) polymer by Degussa. Disadvantages of these precatalysed systems are high costs, limited number of suppliers and the needed high concentration of catalytic material, which has a negative effect on the properties and processing of the polymers. Furthermore, the metallization process is slow because of a low surface concentration (which itself is influenced by the moulding process) of active catalytic sites (nuclei) and requires very active formulas, which are highly instable and require intensive process control [4].

The second method uses a precatalysed polymer, developed by LPKF GmbH, in which the catalytic metal on the surface is locally activated by an UV-laser beam. Main advantage is that a one-shot component, made out of this material, can be provided – in a flexible way - with a fine pitch pattern (defined by laser optics) that may be metallised.

Beside disadvantages related to the use of a highly filled precatalysed polymer and a slow metallisation process, the method requires laser equipment and especially 3-D manipulation of product or laser spot in case of 3-D products, rendering it less suitable for 3-D patterns.

2. New methods for selective metallization

In order to get around bottle-necks in the application of precatalysed polymers, such as the low catalytic activity of nuclei after two shot moulding or laser activation, two new methods for selective metallization of plastics have been developed by TNO, which are based on two-shot moulding and a pre-plating surface treatment [5].

These methods do not involve catalyst compounding to the plastic but can be used on conventional polymer grades. Both methods use conventional electroless (nickel or copper) plating chemistry.

2.1. Selective etching

The first method, selective etching, exploits differences in solubility in an etching or hydrolyzing agent between different polymers [6]. Fig. 1 depicts the process steps. The first step comprises the overall absorption of catalytic Pd. This is followed by selective...
removal of Pd by dissolution of the surface layer of one of the plastics. Then electroless plating follows on Pd nuclei present on the other plastic.

![Diagram](image1)

Fig. 1. Selective etching metallization process, from top to bottom: (i) two-shot moulding, (ii) overall absorption of Pd-nuclei, (iii) selective removal and (iv) selective plating.

This method applies in principle to a wide number of polymer combinations; the optimal etchant must be determined for each combination. This was successfully done e.g. for SPS-PEI (syndiotactic polystyrene - polyethylenimide) and PA4,6-PET (polyamide4,6 - polyethylene terephthalate), for a simple test shape. The PEI respectively PET surfaces could be hydrolysed and dissolved sufficiently (and hence Pd-nuclei removed) in order to plate only the SPS respectively PA4,6 surfaces (see Fig. 2).

2.2. Selective masking

If the not-to-be-plated polymer has a high chemical resistance (is more resistant than the to-be-plated polymer, e.g. for the LCP-PPS (polyphenylene sulfide) combination), the selective etching method will not be applicable. A second approach, selective masking (patent pending), was examined. In this method a differences in surface energy between the two polymers is created, e.g. by alkaline etching in the case of LCP/PPS combination: (see Fig. 3): LCP becomes hydrophilic, PPS (remains) hydrophobic. This allows selective application of a temporary organic film (for example PMMA (polymethyl methacrylate) on PPS, which protects it from absorbing Pd-nuclei and results finally in selective plating of the LCP surface. This method was successfully tried for LCP-PPS and PA4,6-PPA combinations (see Fig. 4).

![Diagram](image2)

Fig. 3. Selective masking metallization process based on selective application of an organic film.

3. Performance tests with a 3D test geometry.

After these feasibility tests, further tests were carried out into the selectivity and reproducibility of the new methods. Because of their commercial availability and importance, the selective etching and selective masking methods tests focused on respectively the PA4,6 - PET and LCP - PPS polymer combination.

The tests were carried out with a complex two shot moulded test object, see Fig. 5. The structure comprises lines/spaces with decreasing dimensions (smallest line width is 500 µm), areas for reflow soldering tests and mounting of a LED, as well as blind and through holes.
3.1. **Selective etching method tests on PA4.6 - PET**

With the selective etching method, a highly reproducible and almost 100% selective (>99%) Cu or Ni-P plating on the PA4.6 substrate is possible - if required with an extra Au layer, for example for soldering purposes, see Fig. 6.

No creeping of fluid between materials occurred: the achieved resolution doesn't depend on the plating process but on the accuracy of the moulding process. This makes this method highly suitable for selective plating of microstructures.

Plating of the through holes is not critical. Plating of the blind holes however needs the addition of a surfactant (surface tension reducing agent) to the Pd-nucleation solution, for improved wetting and metallisation.

Selective plating of Cu on PA4.6 was also possible. Pull mode adhesion tests (carried out with a steel dolly glued to the plated metal layer of dedicated flat samples) showed actually that the Cu and PA4.6 interface was twice as strong as the Ni-P and PA4.6 interface. The fracture stresses were 500 N/cm² versus 250 N/cm². (For comparison, the fractures stress of industrially PVD coated Cu on ABS is in the range of 200 to 300 N/cm²). Almost always, the fracture occurred in the polyamid itself, hence the adhesion depends on the strength of the (etched) surface skin. The lower strength after Ni-P plating, is probably due to the higher metallization bath temperature (90°C for Ni-P versus 52°C for Cu), which may result in a higher water adsorption on the metal-polymer interface.

The application of MID components in the final device often requires these to be suitable for and being able to withstand soldering processes. Hence, soldering tests on Ni/Cu/Ni/Au plated test structures were carried out. With SnAg3Cu0.5 paste, the most widely used lead free solder alloy in the microelectronics industry at present, 0805 resistors were soldered onto the test structures, see Fig. 7. The temperature exposure was chosen according to the Industry Standard IPC / JEDEC J-STD-020C classification test for SnAg3Cu0.5 solder processes [7]. Peak temperature was 237°C, ramp-up and ramp-down rate were 0.6°C/s. The test structure was not (visually) damaged and wetting of tracks and components was good.

3.2. **Selective masking method tests on LCP - PPS**

This method is very successful on the original flat test shapes (see Fig. 4), but appeared to be less stable for the more complicated 3-D test structure. Two aspects were critical (see Fig. 3):

- Complete repulsion of water from the PPS surface after the alkaline etch and rinse step.
- Good breaking and removal of the organic film from (the water coated) LCP surface in the water rinse step prior to the Pd seeding.

The remaining water droplets on the PPS result in local Pd-seeding and hence plating, whereas any remaining film on the LCP causes holes in the metal plating.

The water repulsion from the PPS surface was improved by (i) decreasing the affinity of the rinsing solution with the PPS surface (by increasing its polarity by adding NaCl and its viscosity by adding hydroxyethylcellulose) and (ii) slow removal and insertion of the part into the chemical solutions.

The organic film should break off the surface exactly along the LCP-PPS border. This could be improved (i) by optimizing the film thickness and concentration (thin film is easier to rinse off, but shields the PPS surface less from the Pd-nucleation solution), (ii) by choosing optimal organic film type and molecular weight (effects tearing behaviour and structure). Best results were obtained with a PMMA film of 35,000 Mw.

Fig. 8 depicts the best obtained sample quality. However, its reproducibility remained poor and can probably only improved by automation of e.g. the insertion, removal out of solutions and drying of the parts.
With regard to the adhesion of the plating on LCP, no significant difference in strength between Cu and Ni-P plating was measured. The fracture stresses were 121 Nm⁻² respectively 135 Nm⁻².

4. Conclusions

Two new methods for selective plating of the surface of two-shot moulded components have been proposed and subjected to performance tests. A major advantage of both methods is that these can be applied to conventional polymer grades and use conventional electroless (nickel or copper) plating chemistry.

Conclusions from the performance tests for the first method, selective etching, when applied to a PA4.6-PET combination are:
- The method has a very high selectivity (>99%), a good reproducibility, and a large process window.
- Because of the high selectivity, the plated area is precisely confined by the moulded border between the two polymers. The method is suitable for plating of microstructures.
- The method has a good 3-D performance.
- The plated product withstands industrial lead free reflow soldering conditions.

Conclusions for the second method, selective masking, when applied to a LCP-PPS combination:
- Good performance on simple flat structures but process control is complicated when applied to 3-D structures. This may result typically in unwanted metallized spots on the PPS areas and holes in the plating of the LCP areas.
- Most critical step is the repulsion of water from the PPS surface.
- Industrial application for 3-D features needs stringent process control and automation.

Acknowledgements

This work has been supported by Philips Lighting Vitrite, ITB Precisietechniek and DSM Engineering Plastics.

References