Metallization of Dielectrics Using Conductive Polymer

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Miniaturization of electronics is creating demands for smaller and high density interconnects (HDI) for printed circuit boards (PCB) and packaging. Among direct metallization concepts of PCB dielectrics, the ENVISION® HDI process, has been proven as a highly reliable, productive and environmentally friendly way of manufacturing HDI printed circuit boards.

This paper summarizes new developments and industrially verified improvements of the ENVISION® HDI process for direct metallization. A unique property of ENVISION® HDI is its selectivity. The deposition of the conductive film occurs only on the dielectric and not on copper. This unique feature is preserved in the new developed and more durable HDI process.

Reduced formation of non-conductive oligomers resulting in decreasing quality of the conductive Poly-3,4-Ethylenedioxythiophene-Poly-styrenesulfonate (PEDT) has been improved by addition of a process stabilizer. In addition, process control has been improved by relating non-conductive oligomer contamination to an UV-absorption @ 870 nm.

The developed catalyst “stabilizer”, reduces oligomer absorption at 870 nm and in combination with the development of a new “low temperature “ permanganate initiator, issues related especially to polyimide substrates has been improved significantly. Presented direct metallization improvements are supported by XPS and Auger characterization of the PEDT composition.

Introduction

Intrinsic conductive polymers are characterized by conjugated C-C-double bond structure as in Polythiophene. The DMS-E process is an oxidative polymerization of 3,4-Ethylenedioxythiophene (EDT) in combination with Poly-styrenesulfonic acid (PSSA), acts a precursor for conductive Poly-3,4-ethylenedioxythiophene (PEDT) using MnO_2 as oxidative agent (Figure 1). A detailed description of the process mechanism is given by J. Hupe (1). Depending on bath age, surface topography, substrate and copper plating conditions, typical properties of the conductive polymer film are;

• Electrical resistance	~5 kOhm / 25mm
• Thickness	~120nm
• Thermal Stability	>>400°C
• Lateral Cu-Growth	2-5mm/min

From the chemical principle it’s obvious that a minimum amount of MnO_2 must be present on the dielectric surface to provide the necessary “oxidative potential” for the polymerization reaction. Also obvious too much MnO_2 on the surface than consumed during polymerization is influencing the binding between polymer and substrate, hence reduced adhesion. Between the minimum requirement and the maximum threshold, PEDT conductivity increases linear with MnO_2.

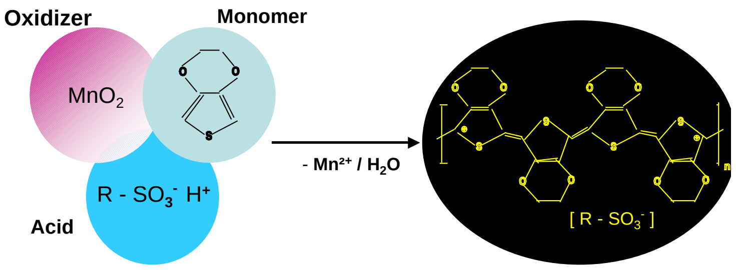

Figure 1. *Generation of Poly-3,4-ethylenedioxythiophene*

Generation of MnO_2 on the substrate surface is a permanganate solution; exposure time and temperature (typically between 80 and 85°C) are key parameters influencing the amount deposited. In addition, with same immersion time and temperature, significantly more MnO_2 is deposited on standard FR4 compared to polyimide substrates.

It's well known that oxidative formation of non-conductive oligomers in the EDT/PSSA solution, the catalyst, is another parameter which reduces PEDT conductivity. As the catalyst ages, measured in days after make-up or processed surface area, the catalyst concentration of oligomers increases and as a consequence oligomers are build into the polymer film creating areas of non-conductivity; PEDT conductivity decreases. At a certain bath age, PEDT quality becomes unacceptable and a new catalyst make-up is required; reduced productivity because of down-time.

In industrial applications, because of production issues, a shelf-time is occasionally required between applying a conductive surface and electrolytic copper metallization. Since conjugated C-C-double bonds are more sensitive to oxidation that single C-C bonds, exposure to ambient air becomes an important aspects to consideration. It's known that PEDT conductivity decreases with storage time, especially on polyimide substrates.

The objective of this R&D study is to develop a more consistent PEDT conductivity versus bath age for both FR4, High Tg and PI substrates during the polymerization itself as well as during a any storage period between polymerization and copper metallization.

Quantification of Conductivity

Catalyst concentration of component A (EDT-Monomer) and component B (PSSA) is controlled by UV-spectroscopy and titration. Various methods for measuring conductivity is in use; resistance, back-light, MnO_2 quantification and lateral copper growth (LCG). In this context only LCG will be used to quantify conductivity. For a comprehensive description of control methodology see Ref. 2.

One method of quantifying LCG is measurement of copper growth on standard FR-4 panels (Figure 2). Test coupons are double sided stripes (100 X 30mm) with 50mm bare laminate exposure at one end (double sided). LCD is measured as the average(a,b,d) (Figure 2, left) after 10 min copper plating @ 1 A/dm^2. Typically, immediately after make-up LCD will be 4-5 mm/min using Cuprostar LP-1 as plating environment (figure 2, left). After 6 days, LCD drops down to around 2 mm/min (Figure 2, right) which as a rule of thumb is the conductivity level where more careful quality control measures must be applied.

In another test vehicle the substrate can be either Standard FR-4, High Tg or PI materials (Figure 3). The test coupon are double side plates (60 x 100mm) with an exposed laminate pattern (windows) on one side and with rows of through holes. LCD is measured as laminate area covered after cu-plate (Cuprostar LP-1 plate, 5 min @ 2 A/dm^2 or 10 min @ 1 A/dm^2).

Typically, first day after make-up 95 % of the exposed laminate will be covered with Copper after plating. Below 40% coverage (Figure 3,right), PEDT conductivity has reached a level where careful quality control measures must be applied.

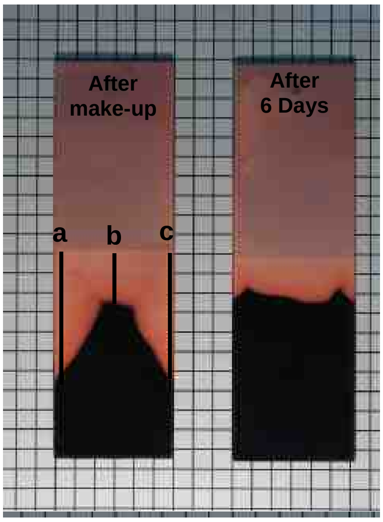

Figure 2. *Standard LCG test coupons A: 4.7 mm/min at day 0 (left) & 2.0 mm/min at day 6 (right). Plating: 10 min. Cuprostar LP-1 at 1 A/dm^2*

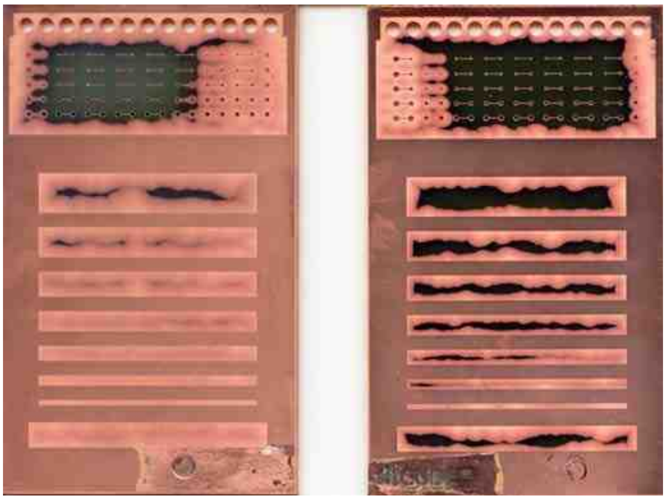

Figure 3*. Standard FR-4 LCD test coupons B: 95% coverage at day 1 (left) &, 40% coverage at day 6 (right). Plating: 5 min. Cuprostar LP-1 at 2 A/dm^2*

Development of Catalyst 7375

The increasing contamination with non-conductive oligomers is easily measured by UV-spectroscopy @ 870 nm absorption. The increasing intensity of this absorption peak as the catalyst ages, correlates well with the observed reduction in LCG-conductivity (Figure 4).

Under laboratory conditions, a stabilizer for the catalyst bath has been developed, which minimizes the formation rate of unwanted oxidation of monomer into non-conductive oligomers. Verification of laboratory results was done in a production environment (Figure 5). The LCG, measured as % Cu-coverage (see Figure 3) using standard Catalyst 7050 reaches the 40% threshold 5-6 days after make-up. The new Catalyst 7375 shows 40% Cu coverage after 14 days, hence ~ 3X bath-life improvement. Parallel to the LCG improvement, contamination with oligomers was reduced. Their concentration levels reached after 3 days for Catalyst 7050, was for the new catalyst 7375 reached after 12 days.

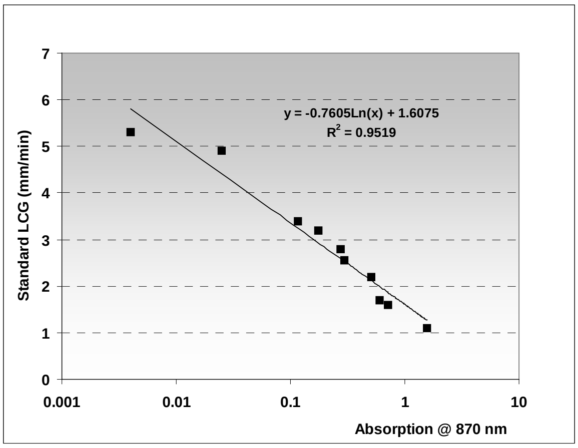

Figure 4. *Correlation between oligomer absorption at 870nm and LCG*

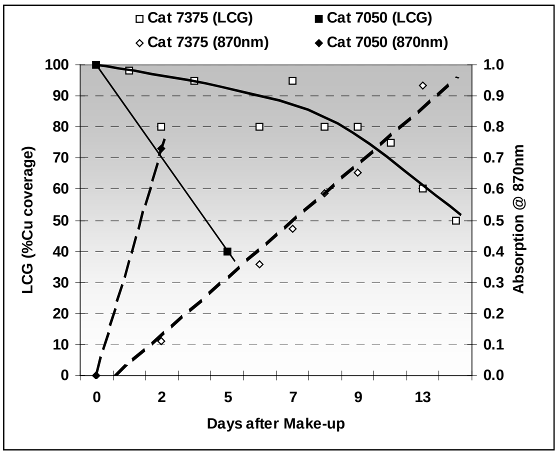

Figure 5. *Catalyst improvement: LCG (■ □), absorption @ 870nm (◆ ◇)*

The reduced formation of oligomers in the catalyst solution after addition of stabilizer improves the ratio between conductive and non-conductive areas in the PEDT film. An XPS analysis showed that the intensity at 157eV was lower for both FR4 (very low ~ 0) and polyimide substrates when processed in this new Catalyst 7375 (Figure 6)(3). The S peak in Figure 6 relates to sulfur from monomer EDT and S^{4+} from PSSA. The test panels was measured a second time after 6 days of exposed to ambient air (simulating storage-time). The XPS analysis revealed that the amount of non-conductive “islands” in the PEDT polymer increased for both substrates and that the intensity peak was similar for both catalysts (Ref. 3 data not shown).

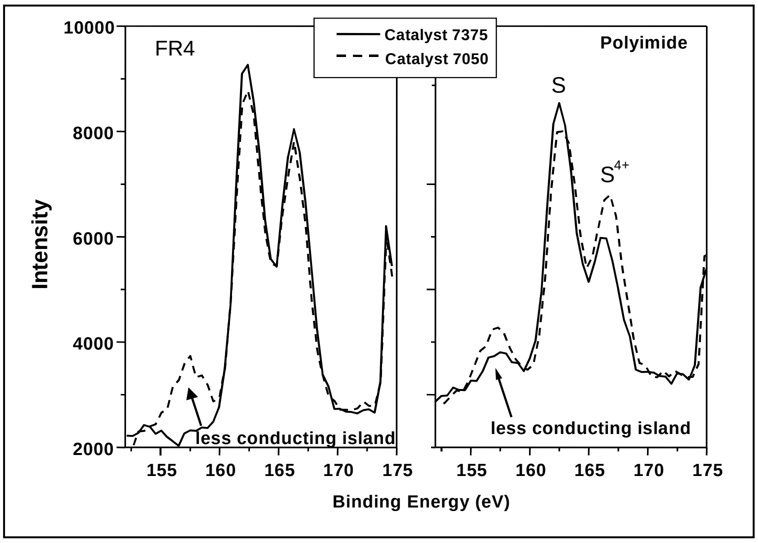

Figure 6. *XPS analysis under e flood gun conditions of PEDT formed in standard Catalyst 7050 and new Catalyst 7375 for FR-4 and PI laminates*

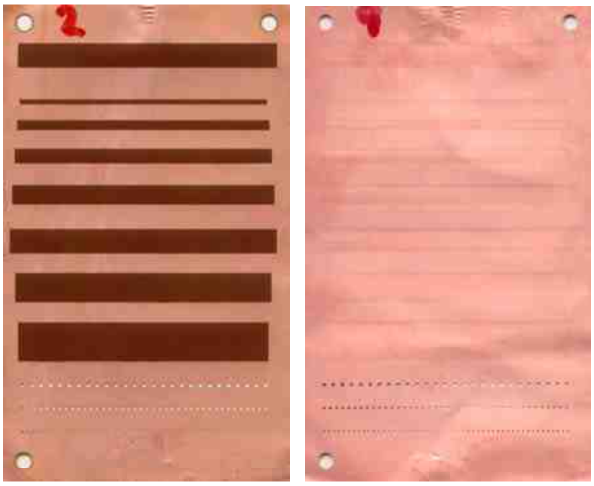

Figure 7. 100% Cu Coverage 36 days of exposure to ambient air: before (left) and after (right) Cuprostar® LP-1 plate 10min @ 1 A/dm^2

It is well known that the PEDT conductivity on polyimide laminates is significantly lower than on standard FR4 and High Tg substrates. Even though the proportion of non-conductivity during processing in the new Catalyst 7375 is reduced for both laminates shown in Figure 6, polyimide still has a higher proportion of non-conductive areas (islands) compared to FR4.

As already mentioned earlier, during permanganate treatment at 80-85°C, compared to standard FR4 laminates, very little MnO_2 is absorbed on polyimide. A new low temperature permanganate Initiator operating from 50-60°C was developed, especially for polyimide substrates. Even though it was developed for PI substrates, the new HDI-Flex Initiator 7325 also works well with standard FR4 & High Tg laminates.

Compared to standard “high temperature” Initiator and standard Catalyst 7050, XPS analysis show increased conductive PEDT film on polyimide, when processed in new “low temperature” Initiator and new Catalyst 7375, and the relative proportion of non-conductive areas is improved significantly; compared to FR4 laminates it increases from “very low” to approximately 25% (Ref. 3 data not shown).

Combining improvements achieved by development of a new low temperature initiator and new life-time improved catalyst, the conductivity of PEDT on polyimide is significantly improved even after extreme prolonged time of storage. During a longer exposure to ambient air, conductivity still decreases, however the improved quality allows for a storage of at least 36 days compared to recommended 3-5 days after “high temperature” Initiator and Catalyst 7050 (Figure 7).

One of the unique properties of using PEDT as a mean of direct metallization is the deposition selectivity. No polymer is formed on copper surface since MnO_2 formation is restricted to dielectric surface. Selectivity during processing PCB laminates in the new “low temperature” initiator and improved Catalyst 7375 is preserved. An Auger analysis show that PEDT is present only on dielectrics substrates since the conductive polymer contains sulfur (Figure 8).

The performance of the new developed initiator (ENVISION® HDI-Flex 7325) and improved catalyst (ENVISION® HDI Catalyst 7375) was tested under production like conditions for multilayered polyimide. After treatment in the “DMS-E” process, laminates was copper metallized in Cuprostar® CVF1. The throwing power of the DC microvia filling process is high and allows it to be used as for Cu-flashing. The deposited copper follows the substrate contour (Figure 9) which is non-uniform

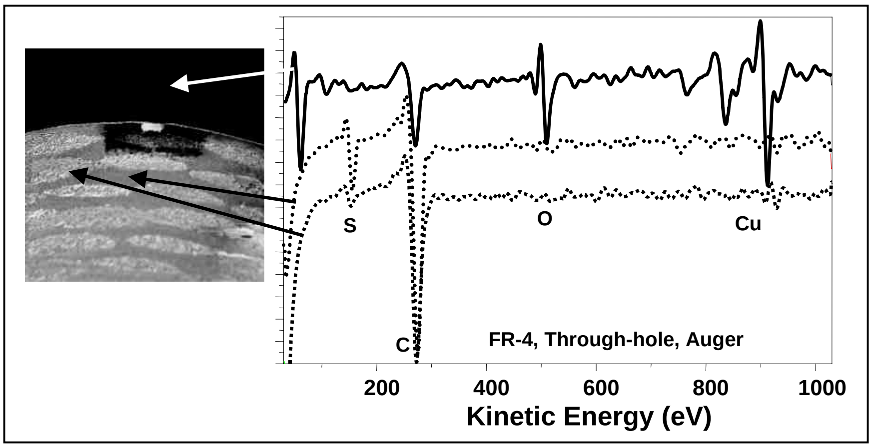

***Figure 8**. Auger surface analysis of standard FR-4. Only sulfur is detected on epoxy and glass fibers. Not on the Cu surface.*

because of the presence of adhesives between the Pi-multilayers (customer quality supplied). After copper flashing, microvia filling and though-hole metallization is made in the presence of process activators. The microvia fill as well and the through-hole PTH (6-point measurement) is 100% and independent on surface topography an even copper plate is achieved in through-holes. In agreement with the Auger results from Figure 8, selective polymer formation is verified by passing 3x Solder Float, 260°C testing.

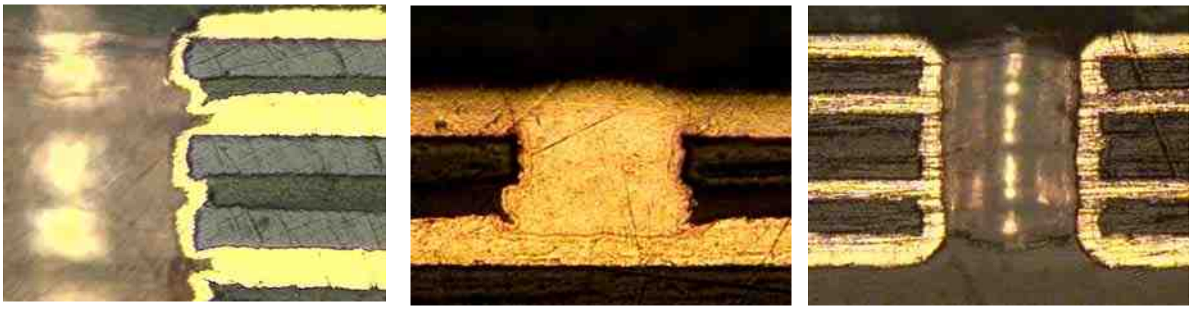

Figure 9. *Multilayered PI-flex: Envision HDI-Flex Initiator 7325 & Envision HDI Catalyst 7375 treatment prior to Cuprostar® CVF1 flash (upper left) followed by 100% microvia fill (middle) and 100% PTH (right).*

Conclusion

Parallel to formation of highly oxidative PEDT, non-conductive oligomers are produced as a byproduct. With increasing contamination of the EDT/PSSA catalyst, PEDT conductivity decreases. Oligomer contamination measured as UV-absorption @ 870nm has been correlated to conductivity measured as LCG. Addition of a catalyst stabilizer has shown that the oligomer contamination rate is reduced and as a consequence PEDT conductivity improved in industrial environment.

Analytical surface analysis of PEDT shows that the improvement is related to a reduced proportion of non-conductive areas, which relates to both standard FR4 and polyamide laminates.

Lowering the MnO_2 temperature after addition of a “promoter” increases the MnO_2 deposition on especially “difficult to treat” PI laminates, hence the PEDT quality is increased. Processing in combination with the new improved Catalyst 7375, extends the PI storage time from recommended 3-5 days to more than 36 days.

The selectivity of ENVISION® HDI is preserved in the new developed direct metallization concept and followed by copper metallization in CUPROSTAR® CVF1, microvia filling and through-hole PTH is 100% and because of selective polymerization, Cu-Cu interface delamination during thermal exposures is preserved.

Literature:

1. Hupe, J.: *“High Reliable and Productive Metallisation Process for Blind Micro Via Applications”*, EIPC, Basel 2005.
2. ENVISION® HDI Quality Control Manual, Enthone TDS document
3. Chen Xu, “*Comparison between Standard 7350 and Catalyst 7375”,* Enthone, SAMPL, Ref. 2826.