POLYPYRROLE-BASED METALLIZATION OF INSULATORS – AN APPLICATION TO PRINTED CIRCUIT BOARDS (PCB)

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Abstract: - The objective of our work is to investigate the application of polypyrrole (PPy) as a conductive precoat for the metallization of PCB holes. The method includes: etching of FR4*, in situ* deposition of a thin film of PPy, resulting in a FR4/PPy electrode. The process is very promising and environmentally friendly compared to the conventional electroless one. Several variables of the process at a laboratory level were studied. The poylyrrole-modified FR4 surfaces were conductive enough to allow the copper plating of the specimens at a later stage. Moreover, the peel strength of the copper plated on FR4 with our method was adequate.

Key-Words: Polypyrrole, PCB, insulators, metallization

1 Introduction

Conducting polymers (CPs) were first produced in the mid-1970s [1] as a novel generation of organic materials that have both electrical and optical properties similar to those of metals and inorganic semiconductors, but which also exhibit the attractive properties associated with conventional polymers, such as ease of synthesis and flexibility in processing.

Polypyrrole (PPy) is one of the most widely used conductive polymers, due to its high chemical and physical stability, low toxicity of the monomer and its easy chemical or electrochemical synthesis, even in aqueous solutions [2, 3, 4]. PPy may be prepared by chemical or electrochemical oxidation. It has been proven that by inserting doping anions (Figure 1) like PTS (para-toluene-sulfonic acid) the conductivity of PPy can be increased up to 10^2 S/cm, [5, 6, 7].

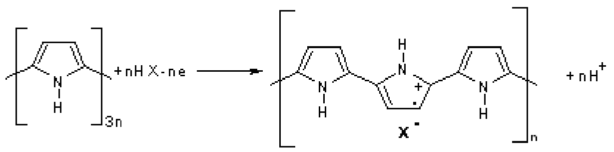


Figure 1 – Doping mechanism of PPy

Applications of PPy were essentially extended during last years and include now such different fields of science and technology as corrosion protection of metals, development of individual electronic devices e.g. diodes, metallization, electromagnetic interference shielding, biosensors, tissue engineering scaffolds, neural probes, drug-delivery devices, and bio-actuators[8, 9,10].

2 Problem Formulation

In microelectronics, printed circuit boards (PCBs), are used to mechanically support and electrically connect electronic components using conductive pathways, or trace*s*, etched from copper sheets laminated onto a non-conductive blank fiberglass substrate ("the board"). There are many types PCB substrate material, but by far the most common is a standard woven epoxy glass material known as FR4. The complexity of PCBs, vary from single-sided boards, where circuitry is found on only one side, to double-sided boards, to boards comprising several layers of circuitry. Connections between the two sides of a board and layer-to-layer connections are made with copper-plated through-holes (PTHs) [8].

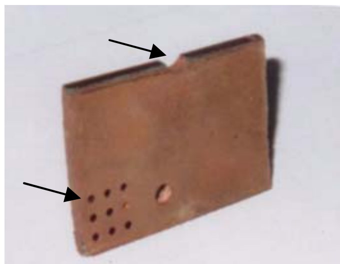


Figure 2 – PCB through-hole copper plating with PPy used as a precoat (pretreatment)

The through-holes are drilled into the laminated substrate and are then copper-plated (Figure 2).
The introduction of double-sided, followed by multilayer boards, was achieved by metallization of the drilled holes with electroless copper. Autocatalytic electroless copper plating has been successfully used for over 30 years. However, this process has certain disadvantages [11].
Firstly, electroless deposition of copper requires a reducing agent. Formaldehyde, the most commonly used reducing agent in electroless baths is toxic and poses environmental concerns. Secondly, electroless baths are generally unstable and require close monitoring. Control becomes a problem and cyanide and chelating agents have to be added, which in turn are difficult to remove from waste streams [11].
In addition to the environmental concerns about electroless copper metallization, circuit board manufacture using this process requires the use of expensive noble-metal salts, such as $PdCl_2$ and as many as 8- 10 steps (including rinses).The inherent disadvantages of the electroless copper metallization fostered interest in direct metallization of copper. There are processes in which the activation of the non-conducting wall of the PCB holes is effected by deposition of carbon particles or conductive polymers [11, 12].

3 Problem Solution

The aim of the present study is to investigate the application of polypyrrole (PPy) as a conductive *in situ* precoat for the metallization of PCB holes Several variables of the process at a laboratory level were studied.
In particular, the effect of the substrate pre-treatment (H_2SO_4) and the polymerization bath synthesis (addition of KOH) on the peel strength of copper on the FR4/polypyrrole electrode was evaluated. An assessment of the peel strength of the copper plating was performed. Furthermore, the interface and the thickness of the copper electrodeposited was studied by SEM/EDS analysis.

3.1 Materials and Methods

Firstly, FR4 specimens (2,5 x 2,5 cm) were etched by immersion for 30 min in a firmly agitated aqueous solution containing 8% pv $(NH_4)_2S_2O_8$. Ammonium persulfate acts as an oxidant in the polymerization of pyrrole. PPy is polymerized on FR4 surface, from an appropriate optimized solution that contains 3.6% pv pyrrole and 4.4% pv. PTS that acts as a dopant [10]. Thus, a new electrode is formed that can be electroplated.
The FR4/PPy electrode has been electroplated using the electrolytic cell that contained a copper ion bath. The composition of the copper deposition bath was: 150 g/L $CuSO_4*5H_2O$, 50 g/L H_2SO_4, 50 g/L CH_3CH_2OH (EtOH). Copper was deposited onto FR4/PPy surface resulting in the formation of a FR4/PPy/Cu sample. After being covered with PPy film, FR4 specimens were immersed in $AgNO_3$ 0,1 N solution for 10 min before metallization started.
During the copper electrodeposition of FR4 substrates the current density and the metallization time were recorded.
The peel strength of copper coating (Cu) on the polypyrrole-modified FR4, was measured according to ASTM-B-193-02 specification. SEM/EDS analysis of the copper coated FR4 specimens was performed.

3.2 Results – Discussion

In a previous work we have tested the adhesion of copper layer on ABS specimens according to the ASTM D 3359, method B (“Cross-Cut Tape Test”) [2]. It has been demonstrated that the peeling of the copper coating is caused by the poor adhesion of the PPy film on ABS [12].
For this reason, we attempted to increase the peel strength of PPy on the FR4 substrate by (a) chemical treatment (etching) of the specimens with H_2SO_4 and (b) addition of KOH in polymerization solution.

A. Treatment with H_2SO_4

Figure 3 shows the peel strength (lb/in) as a function of etching time (min).

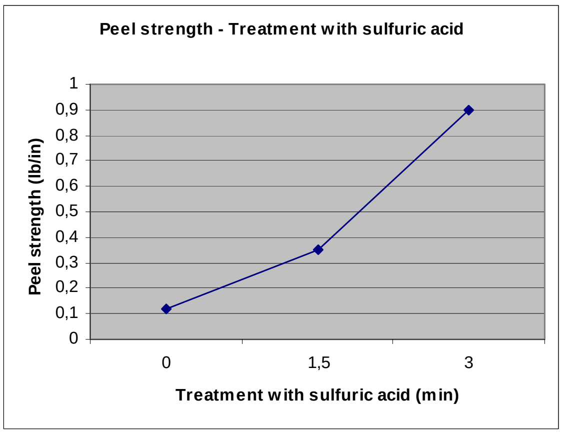


Figure 3 Peel strength of copper on FR4 (lb/in) vs. etching time (min).

Peel strength of 0.90 lb/in was reached after pre-treatment with sulfuric acid for 3 minutes (Figure 3). Therefore, the etching of the substrate with H_2SO_4 has significantly increased the peel strength.
This can be attributed to the poor acid resistance of epoxy resins that results in an increase of the surface roughness.

B. Addition of KOH to the polymerization solution

Adding dropwise 6% w/v KOH to the polymerization solution results in a significant increase of the peel strength from 0.29 lb/in to 0.35 lb/in.
SEM/EDS analysis of two groups of polypyrrole-modified FR4 copper plated specimens: Group A: without KOH addition and Group B: with KOH addition

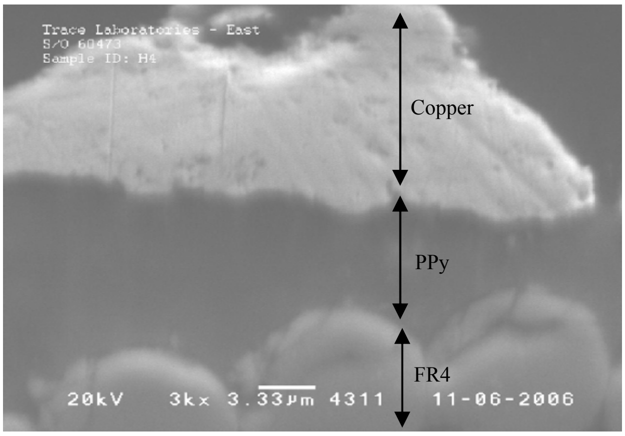
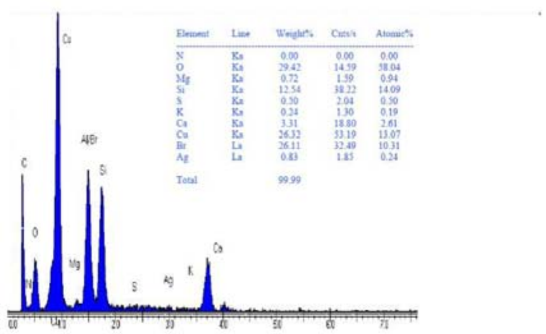


Figure 4 Group A specimen (representative cross-section view)

The polypyrrole conductive layer (interface) was not of equal thickness and ranged from 4.5 μm to 9.65 μm (Figure 4). Additionally, in figure 5, EDS analysis of a Group A specimen is shown.



Element	Line	Weight%	Cnts/s	Atomic%
N	Ka	0.00	0.00	0.00
O	Ka	29.42	14.59	58.04
Mg	Ka	0.72	1.59	0.94
Si	Ka	12.54	38.22	14.09
S	Ka	0.50	2.04	0.50
K	Ka	0.24	1.30	0.19
Ca	Ka	3.31	18.80	2.61
Cu	Ka	26.32	53.19	13.07
Br	La	26.11	32.49	10.31
Ag	La	0.83	1.85	0.24
Total		99.99		

Figure 5 – EDS analysis of a Group A specimen.

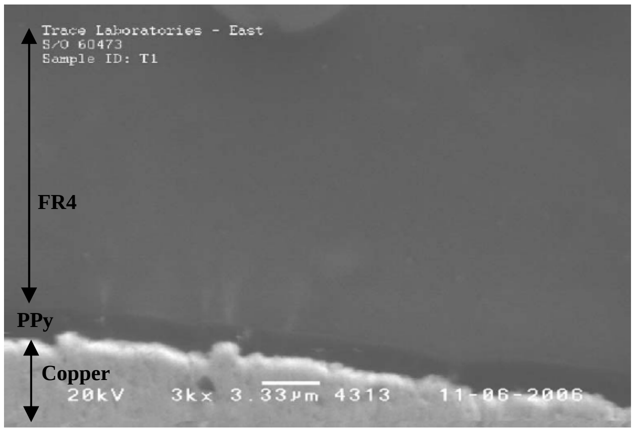
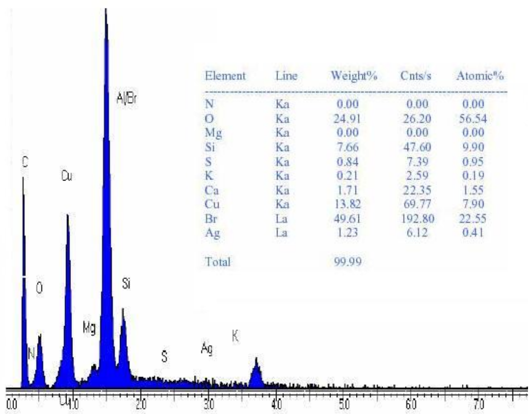


Figure 6 Group B specimen (representative cross-section view)
As it is shown figure 6, the PPy layer was more uniform with a thickness equal to 1.88 μm. The EDS analysis of the specific specimen is demonstrated in figure 7.



Element	Line	Weight%	Cnts/s	Atomic%
N	Ka	0.00	0.00	0.00
O	Ka	24.91	26.20	56.54
Mg	Ka	0.00	0.00	0.00
Si	Ka	7.66	47.60	9.90
S	Ka	0.84	7.39	0.95
K	Ka	0.21	2.59	0.19
Ca	Ka	1.71	22.35	1.55
Cu	Ka	13.82	69.77	7.90
Br	La	49.61	192.80	22.55
Ag	La	1.23	6.12	0.41
Total		99.99		

Figure 7 EDS analysis of a Group B specimen

EDS analysis results (Figures 5 and 7) clearly demonstrate that the addition of KOH reduces the mass of Cu deposition. This finding is in agreement with the reduced Cu film thickness deposited on Group B specimen as revealed by SEM.

4. Conclusions

Within the limitations of this study, the following conclusions can be drawn:

- The FR4/PPy electrode has sufficient conductivity to allow the copper plating
- Using H_2SO_4 as an etching agent increases the peel strength of the copper coating on the substrate up to 0.90 lb/in. This may be attributed to the roughness increase of the FR4 surface.
- The addition of KOH to the polymerization solution also increased the peel strength of

copper on FR4. However, it reduced the mass of deposited Cu.

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