



# Surface modification of an epoxy resin with polyamines and polydopamine: The effect on the initial electroless copper deposition

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## ABSTRACT

This paper describes the influence of polydopamine and polyamine surface modifications of an etched epoxy cresol novolak (ECN) resin on the initial electroless copper deposition. Three different strategies to introduce polyamines on a surface in aqueous environment are applied: via polyethyleneimine adsorption (PEI), via polydopamine and via polyamines grafted to polydopamine. Next, the influence of these surface modifications on the catalytic palladium activation is investigated through X-ray photoelectron spectroscopy (XPS) analysis. Finally, the initial electroless copper deposition on modified epoxy surfaces is evaluated using SEM and Energy Dispersive Spectroscopy (EDS). Grafted polyamines on polydopamine surface modifications result in a large increase of the initial deposited copper.

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## 1. Introduction

Electroless copper deposition on polymers is used for a variety of applications ranging from decorative elements to high-tech electronic components and printed circuit boards (PCBs) [1,2]. In the case of PCB manufacturing, the production of high density interconnects for integrated circuits (ICs) require additional sequential build-up (SBU) layers [3–5]. Good adhesion between the deposited copper and the dielectric layers (epoxy resins) is a key issue for the reliability of these copper interconnections. In most cases, epoxy resins are roughened using strong oxidizing aqueous solutions to increase the adhesion toward electroless copper through mechanical interlocking [4]. Nowadays, the evolution of the microelectronics industry is guiding toward higher density substrates with smaller features requiring dielectrics with a minimum amount of roughness [6–8]. Therefore, chemical modification of epoxy resin surfaces can compensate the loss of mechanical adhesive strength.

During the past three decades, intensive research was performed on surface modifications of polymer substrates to increase the adhesion toward electroless deposited metals. For this purpose, several surface modification techniques were applied such

as wet-chemical [8,9], plasma [10–13] and plasma induced-graft (co)polymerization [14,15]. Generally, the introduction of nitrogen containing functional groups, especially amines, on polymer surfaces revealed the largest potential for adhesion improvement. Out of this reported research, it became clear that an increase and/or the control of the amount of Pd(0) on the surface after catalytic activation plays a crucial role during subsequent electroless copper deposition [10,12,16]. Palladium containing solutions or colloidal dispersions can be used to activate the surface catalytically prior to the introduction in an electroless copper plating bath. During the initial phase of electroless copper deposition, Pd(0) catalyzes the oxidation of an organic compound (e.g. formaldehyde) which reduces the Cu(II) to Cu(0) on the substrate surface [17]. Three types of activation methods can be used for this pretreatment: two step, one step and palladium chloride solutions. More information on these activation methods can be found in literature [17]. During these activations, two possible types of interactions between palladium (in the complexed form) and the amine modified surfaces have been reported: covalent (coordinative) and ionic bonds [10,16]. Ionic bonds can be established between negatively charged palladium complexes or colloids (in an acidic medium) and protonated amines.

A straight forward method to introduce polyamines on the surface of polymers consists of the application of a polydopamine coating. This polydopamine modification method was introduced

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by Messersmith et al. in 2007 [18]. The polydopamine coating was inspired by the chemical structure of mussel adhesive proteins. A large variety of substrates (polymers, ceramics, metal oxides, metals...) can be modified using this method. This polydopamine modification method can be applied by simply introducing a substrate in an aqueous marine solution (pH 8.5) followed by addition of dopamine. The thickness of this layer varies from 5 to 50 nm [19]. From a chemical point of view, it is assumed that the polydopamine layer contains amine, quinone, 1,6-dihydroxyindole and catechol functional groups [20]. Therefore, increased adhesion toward metals can be expected. Moreover, it has already been reported that polydopamine modified polymers reveal increased adhesion toward MOCVD (metalorganic chemical vapor deposition) [21] and electroless deposited copper on polymer substrates [8].

Polydopamine modified surfaces can also be used as a versatile platform for secondary modifications which can further tailor the surface chemical properties [20,22]. An important secondary modification consists of introducing (bio)macromolecules which contain a nucleophilic group (R-N-H<sub>2</sub>, R-S-H) via Michael addition or Schiff base reaction. Doing so, macromolecules can be grafted on the polydopamine layer. This method is used extensively to tailor surfaces for specific cell interaction/proliferation [23,24]. This strategy will be applied here to introduce polyamines on polydopamine modified surfaces.

In this work, three different surface modifications in aqueous media are performed to influence the Pd(0) surface concentration after activation. The modifications are performed on mildly etched ECN resin surfaces. The first method is a simple adsorption of PEI in aqueous solutions. The second method consists of modifying the surface with polydopamine. The third method uses the above mentioned grafting-on method to introduce PEI and diethylenetriamine (DIEN) on the substrate surfaces.

In a second phase, the modified surfaces are introduced in a Pd colloidal dispersion (one step activation method). The influence of these modifications on the palladium surface concentration and oxidation state is analyzed with XPS. Next, the activated substrates are introduced in an electroless copper deposition bath for a short amount of time. The initially deposited copper is evaluated by SEM and quantified with SEM-EDS. Finally, the influence of the surface modifications on the electroless copper deposition is discussed.

## 2. Experimental

### 2.1. Materials

Branched PEI (M<sub>w</sub> 25,000 g/mol), DIEN, linear PEI (50 wt% in water, M<sub>w</sub> 1200 g/mol), TRIS (trisaminol) and dopamine.HCl are purchased from Sigma Aldrich and used as received. MilliQ water is used for solution preparation and all rinsing steps. Probelec XB 7081<sup>TM</sup> is provided by Huntsman<sup>TM</sup>. Probelec XB 7081 is a liquid photo imageable dielectric. It contains an epoxy cresol novolak (ECN) prepolymer dissolved in 1-methoxy-2-propylacetate, a cationic photo-initiator and different types of filler materials [6]. The Circuposit<sup>TM</sup> products are purchased from Rohm and Haas.

### 2.2. Preparation of a mildly roughened ECN resin on FR4

Probelec XB 7081 is dip-coated on an FR4 substrate (10 cm × 10 cm; 1.2 mm thick). Next, this substrate is submitted to different drying, illumination and curing steps as described previously [6]. The final layer has a uniform thickness of about 40 μm. Roughness is introduced by 10 min swelling followed by chemical etching at 80 °C (1, 1.5 or 2 min) in Circuposit Hole Prep

4425 and KMnO<sub>4</sub>/NaOH (Circuposit 3310) solutions, respectively [8].

Prior to the surface modification reactions, all ECN resins are etched in a hot KMnO<sub>4</sub>/NaOH aqueous solution for relatively short times (maximum 2 min). This results in a pore type roughness on the ECN surface. This process and the surface characteristics have been described previously [6].

### 2.3. Surface modifications of a mildly roughened ECN resin

The procedure for the adsorption of branched and linear PEI is performed by inserting an ECN sample in a 2 wt% aqueous solution of PEI for 24 h. Prior to the modification reaction, the pH of this solution is adjusted to 7 using a 0.1 M HCl solution.

The surfaces of the ECN resins are modified with polydopamine using the procedure described by Messersmith et al. [18]. A Tris-HCl buffer solution is prepared at pH 8.5. Next, the substrates are inserted in this solution. Finally, 2 g/mL of dopamine is added and the reaction mixture is stirred slowly under ambient air for 24 h.

Branched and linear PEI, and DIEN are grafted on the polydopamine by inserting the polydopamine modified substrates in a PEI aqueous solution for 1 or 24 h. This solution contains 5 g/L of polyamine and 10 mmol/L of Tris (pH 8). After all modification reactions, the modified samples are rinsed twice in water for 10 min followed by drying using nitrogen blowing.

### 2.4. Catalytic activation and electroless copper deposition

Electroless copper is deposited on (modified) substrates via the 1-step Shiple process. In this process, the substrate passes through different baths. Apart from the rinsing steps in water, Pre-dip 3340, Catalyst 3344 and Circuposit 3350-1 solutions are used for activation and plating respectively. The solutions are made-up according to the technical data sheets provided by Rohm and Haas. An overview of the full process is presented elsewhere [8].

The catalytic activation is performed by inserting the samples for 1 min in the Pre-dip solution. Next, the samples are immersed for 4 min in the Catalyst 3344 bath at 35 °C. Finally the samples are inserted in DI water for 2 min at RT and rinsed with copious amounts of water. After drying by nitrogen blowing, the samples are stored under nitrogen atmosphere.

The electroless plating step is performed in a Circuposit 3350-1 solution with air agitation. The bath temperature is 35 °C. In order to study the initial electroless copper deposition, the immersion time in the electroless copper bath is limited to 45 s. After plating, the samples are rinsed with copious amounts of water, followed by nitrogen dry blowing. Finally the samples are dried in a convection oven at 150 °C for 1 h.

### 2.5. SEM and SEM-EDS analysis

Scanning electron microscope (SEM) analysis is performed on a JEOL JSM-5600 instrument. The SEM analysis is performed using a secondary electron detector or a back scattered electron (compositional contrast mode) detector. The SEM instrument is equipped with an electron microprobe JED 2300 and an EDS (Energy Dispersive Spectroscopy) detector for elemental analysis. Prior to analysis, all samples are coated with a thin gold layer (circa 20 nm) using a plasma magnetron sputter coater.

In case of the SEM-EDS analyses, samples are analyzed in the “mapping mode”. Each sample is measured on three random spots of 200 μm × 250 μm. The elemental composition of the analyzed volume is determined using the “Phi-Rho-Z Quantitative Analysis Software” purchased from JEOL. The copper concentration is determined as the wt% of copper. The total wt% is composed of

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