Surface Characteristics of Ink-Jet Printed Circuits by Polyelectrolyte Multilayers with Zone Model Analysis and Salt Solution Improvment

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Abstract

This paper disclosed recent novel development in printing circuit on flexible substrate by combining self-assembled polyelectrolytes, inkjet printing of catalyst, and electroless plating of metal. Experimental results indicated that building up zone model would enhance substrate surface uniformity. The results also showed that salt concentration would dramatic change the polyelectrolyte layer property before ink-jet printing of catalyst. Salt ions would balance charges in polyelectrolyte layers and smear the surface.[1] *It made the finer diameter of porous hole and significantly increased the adhesion between the ink-jet catalyst and the substrate. Surface uniformity was controlled within ±5%. A high quality circuit fabricated by said ink-jet printing method is presented.*

Introduction

In recent years, the layer-by-layer deposition of polyelectrolytes on charged surfaces has been established as a highly successful and versatile technique for tailoring surface properties of thin film. The electrostatic interaction between charged polyelectrolytes and surfaces of opposite charge causes adsorption of the polyelectrolyte from aqueous solution and leads to surface charge reversal, enabling further alternate adsorption of positively and negatively charged polyelectrolytes. The films may undergo charge density morphological reorganizations.[2]

The multilayer thin film composed of two simple polyelectrolytes, an anionic homopolyelectrolyte and a cationic homopolyelectrolyte, was that of a film subdivided into three distinct zones. The first layers being deposited close to the substrate, they will possess a slightly different structure as the region of bulk film (core zone or zone II). Typically the thickness per layer in zone I was slightly smaller than that in zone II. In zone II film properties were constant. When approaching the outer part of the multilayer, the local properties should again vary because of the solution environment. The outer region over which the local film properties were no longer similar to those in zone II constitutes the outer zone of the film, or zone III. It should be clear that the transitions between zones I and II and between zones II and III are gradual. When the film was fabricated, zone I was completed first. As more layers were added zones I and III will preserve their respective thicknesses while zone II will grow in thickness. One could describe this in the following way, the new layer will adsorb on the surface, and thus the transition zone between II and III will move up by one layer as well. While zone II should swell when exposed to salt solutions as the salt will break ionic bonds between polyanions and polycations. In contrast, the layers in zone III should not be charge compensated and thus show classic polyion like behavior. This means that they should swell in pure water and collapse in salt solutions owing to the screening of the electrostatic repulsion between charges of equal sign.[3]

The swelling and de-swelling in solutions of salt and pure water may have an annealing effect on the film. When salt was diffusing into the film then presumably some of the inter-chain ionic bonds open up. These bonds would close when the salt diffuses out of the film again, but the closure may take place with different counterion partners, thus removing some strain as the polyion chains can adapt to a more equilibrated structure. The idea was that, in the presence of salt, the local mobility of the chain was enhanced and the more equilibrated structure was stabilized again after rinsing with water. There was only indirect evidence for this annealing; it was observed that the surface roughness of multilayer films of poor quality could be improved by cyclic immersion in salt and water to values typically observed with samples of good quality.[4,5]

In this paper, we report a method to modify PEMs surface characteristics, analyze the polyelectrolyte layer building behavior, This result can further combine with ink-jet printing of catalyst and electroless plating for fabrication electrical circuits.

Experimental Section

Multilayer Assembly

Poly(allyamine-hydrochloride)(PAH)(Mw=55000~65000) and Poly(acrtlic-acid)(PAA)(Mw=70000, 25% aqueous solution) were obtained form Aldrich. All chemicals were used without further purification. Deionized water was exclusively used in all aqueous solutions and rinsing procedures. The concentration of the polyelectrolyte dipping solutions was 10mM based on the molecular repeat unit of the monomer. The pH of the PAH solutions was adjusted to 7.5 by adding 1M HCl and PAA solutions was adjusted to 3.5 by adding 1M NaOH. The salt concentration was adjusted by adding NaCl. Layer-by-Layer dipping was carried out auto-dipping machinery.

Ink-Jet Printing

A PZT ink-jet printer was filled with catalyst in DI water. Printing can be done primarily on polyimide, FR-4 substrate with different self-assembly layer pre-process. The printing pattern can accord to the input of image data. When dried, the catalyst will be adhesive on the substrate surface, and diffusing onto the monolayer of poly (allylamine hydrochloride) (PAH). It makes a pattern on the substrate.[6,7]

Table 1: The Process Flow of Self-Assembled Polyelectrolyte

Step	Conditions
Substrate Cleaning	1.Toluene and 2.DI-water washing
Immerse into PAH$_{(aq)}$	PAH$_{(aq)}$ (10mM)
Substrate flushing	DI-water
Immerse into PAA$_{(aq)}$	PAA$_{(aq)}$ (10mM)
Repeat(PAH/PAA) Bi-layers Structure	Up to three bi-layers of PAH / PAA outmost was PAH
Last immersed into PAH$_{(aq)}$ (10mM)	PAH$_{(aq)}$ (10mM)

Electroless Plating

Before electroless copper process the substrate need dipping the accelerator solution 3~10s then washing with DI water.. All of the reagents were dissolved in DI water at room temperature and stirred. To keep the solution stable, a bubble generator with air was used in the plating bath. The pH of the bath was monitored in specific pH value, and the copper deposition carried out at 40℃. Immersion time and temperature are two key factors to control the wire thickness. After removal from the plating solution, the samples were rinsed with DI water to remove loose copper and plating solution and then set aside to dry.[6,7]

Result and Discussion

Zone Model

Figure 1 shows water droplet advancing contact angles measured on the series of multilayer films fabricated with PAH. When the contact angle decreases suddenly, that was the zone model as we defined this layer. Zone I (the layers between solid support and the core zone (zone II)) of FR-4 was composed of approximately a three bi-layer with outmost layer being PAH. And the zone I of Polyimide was composed of approximately a six bi-layer with outmost layer being PAH. Keep increasing the bi-layers structure has not significant change in surface property. Figure 2 shows contact angle of a six bi-layer PAH and PAA outmost was PAH on polyimide thin film, the contact angle uniformity was excellent on the polyimide thin film and control within ±5%.

Salt Induced

The onset of swelling and shrinking is visually detected by a change in the film's surface structure. This changed in the AFM image of (a) a typical non-porous bi-layer PAH/PAA outmost was PAH film prepared from polyelectrolyte solutions without salt. (b) a six bi-layer PAH/PAA outmost was PAH film prepared from polyelectrolyte solutions containing 0.1M NaCl could emerge the surface difference. In figure 3.the film (a) was laterally homogeneous with no distinct surface feature. In contrast, a remarkable increase in surface roughness is found for the multilayer deposited from salt-containing solutions and washed with pure water after deposition of each layer. Figure 3. (b) showed the morphology of a bi-layers outmost was PAH Polyelectrolyte film prepared from PAH and PAA solutions containing 0.1M NaCl and with pure water washing after each layer was adsorbed. This film shows the roughness development could be controlled if a solution of salt concentration equal to that from which the polyelectrolyte were adsorbed.

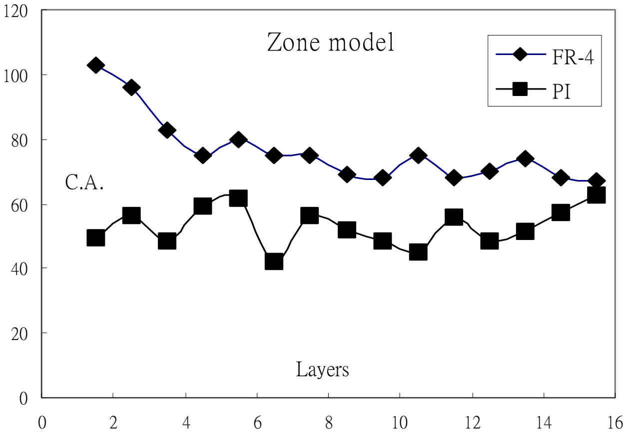

Figure 1. The zone model was building up for a three bi-layer PAH/PAA outmost was PAH film on FR-4 and a six bi-layer PAH/PAA outmost was PAH film on PI.

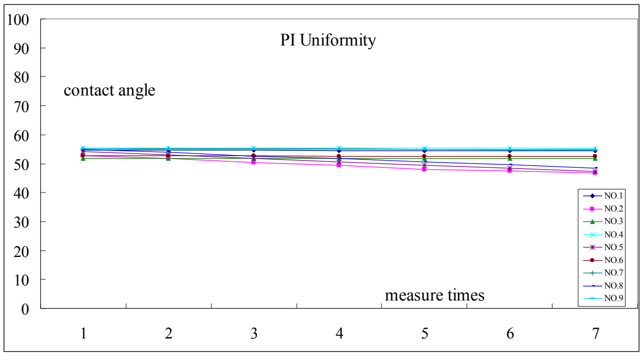

Figure 2. Advancing contact angle data was between 50~60±5°for a six bi-layer PAH and PAA outmost PAH of PI substrate.

Sample Verification

IPC 6013 covers qualification and performance requirements of flexible printed wiring. In this standard, the flexible printed wiring may be single-sided, double-sided, multilayer, or rigid-flex multilayer. To verify the adhesion capability between with and without salt process, the 3M-tape peeled at vertical direction presented excellent adhesion between circuit and flexible substrate no trifles left at tape was observed. Figure 4(a) and 4(b) showed the adhesion capability between copper wire and polyimide substrate without and containing salt process. It was obviously that the salt process has significant promotion in adhesion.

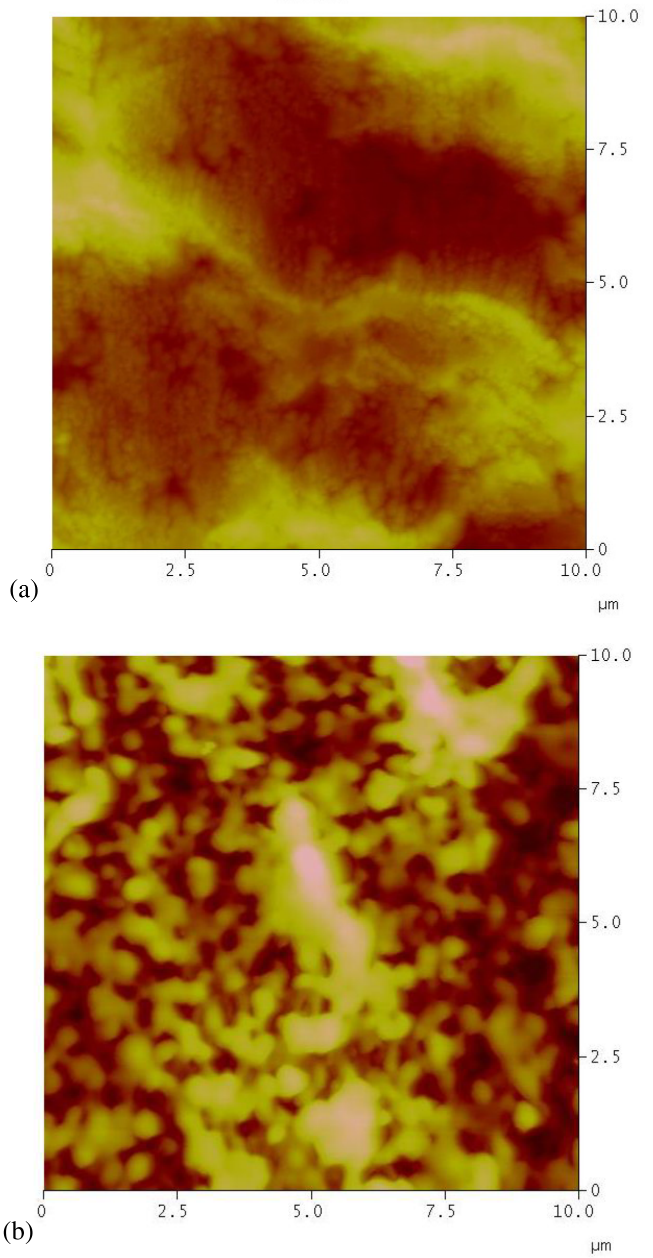

Figure 3. AFM image of (a) a six bi-layer PAH and PAA outmost was PAH film prepared from polyelectrolyte solutions without salt, following by washing with pure water after deposition of each layer. AFM image of (b) a six bi-layer PAH and PAA outmost was PAH film prepared from polyelectrolyte solutions containing 0.1M NaCl, following by washing with pure water after deposition of each layer.

Conclusions

The influence of the zone model and salt induced structure charges in multilayer of polyelectrolyte would modify substrate surface properties. The PAH and PAA zone model on polyimide was a bi-layer outmost was PAH. By measuring the contact angle, a significant drop occurred at 3.5 bi-layers for FR-4 substrate and about 6.5 bi-layers for polyimide substrate were observed. It implied the evidence of full zone (Zone I-III) has been established. In this range, the surface uniformity was controlled within ±5%. A 0.1M salt concentration would change the polyelectrolyte layer properties before ink-jet printing of catalyst. Salt ions would balance charges in polyelectrolyte layers and smear the surface. It made the finer diameter of porous hole to enhance surface the adhesion between the ink-jet catalyst and the substrate. Experiments found the salt process was helpful for improving surface property and it results a excellent adhesion capability passed IPC 6013 standard.

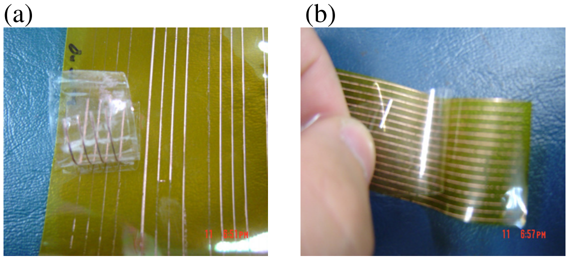

Figure4. 3M tape adhesion capability test (a) without salt, the metal wire would stripped in the 3M tape test. (b) Containing salt, the metal wire would not stripped in the 3M tape test.

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Author Biography

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