Circuit Fabrication by Ink jet Printing on Hybrid-Multilayer Polyelectrolytes

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Abstract

Polyelectrolyte multilayers (PEMs) fabricated by the layer-by-layer adsorption of cation and anion polyelectrolyte solution are used to modify the properties of the substrate and to improve adhesion for electroless plating. In this paper, a fabrication process of specific membrane that consists two kinds of polyelectrolytes adsorption was successfully improving surface property. This membrane combines PAA/PAH and PSS/PAHlayers. The inner layers, PAH/PSS layers, supplied a uniform and higher contact angle porous film. The outmost layer, PAA/PAH layer, provided available surface to react with Pd-complex which is printed by Ink-Jet. Through these treatment processes, we can obtain high performance metal circuits after printing of catalyst and then electroless plating deposition. In addition, we have demonstrated the feasibility of layer by layer polyelectrolyte multilayers for surface treatment, and the catalyst layer patterned by ink-jet method.

Introduction

Classical PCB processes include the steps of dry metal film attached to substrate, spinning photo resist, mask patterning & development, etching photo resist, the second metal plating, and cleaning resist etc. complex processes. For many years, screen-printing and photolithography have been the predominant methods of imaging in PCB manufacturing processes. In recent year, non-photolithographic approaches to preparing patterned catalytic surfaces for electroless plating to form the circuits have been developed. Micro contact printing (μCP)[1] and ink jet printing (IJP)[2] tools are corroborated to appropriate for this PCB process. However, the main drawback, the stability of catalyst and printing quality and adhesion of the electrolessly plated metal were strongly dependent on the surface material.

Polyelectrolyte multilayers (PEMs) are thin films formed from two oppositely charged polyelectrolytes, alternately adsorbed onto a surface one layer at a time. Due to the higher surface area and the micro-porous structure forming,[3] these self-assembled polyelectrolyte layers are of great benefit to the adsorption of the catalyst used for metal deposition. Decher et al.[4] described a layer-by-layer self-assembly method for the fabrication of multilayer thin films which is principally based on the self-diffusion process. Polyelectrolyte chains are adsorbed onto an oppositely charged surface owing to the electrostatic attraction.

Ultra thin multilayers film is currently gaining in many areas such as integrated optics, electronics, light-emitting diodes, photovoltaic, optical sensors or surface orientation layers.[5-9] Most of these applications require preparation of stable and well-organized films with fast fabrication processes.

Cho et al.[10] described a spin self-assembly method as an alternative for making well-organized multilayer films in a very short process time. This novel process is much simpler and faster than the conventional dipping process. Schlenoff[11] studied the polyelectrolyte multilayers (PSS/PDAD) deposited by sequential spraying processes. They found the morphology, uniformity, and chemical compositions of sprayed multilayers, as well as the selective membrane properties were virtually identical to those prepared by dip-immersion. Actually, some polyelectrolyte solutions have the physical properties near pure water, like PAA and PAH, are suitable to form pattern by ink-jet method.[12,13]

In this paper, a fabrication process of specific membrane that is received by two kinds of polyelectrolytes adsorption was successfully adverted. This membrane combines PAA/PAH and PSS/PAH regions. The inner layers, PAH/PSS layers, are supplied a uniform and higher contact angle porous film. The outmost layer, PAA/PAH layer, can provide available surface to react with Pd-complex, which is printed by Ink-Jet. Through these treatment processes, we can receive find and high performance metal circuits after printing and electroless deposition. In addition, we attempt to finish all the processes include the layer-by-layer polyelectrolyte multilayers, and the catalyst layer is patterned by all ink-jet method.

Experiments

Ink-Jet Platform

The ink jet system consists of a specially designed ink jet head for patterning. The head has 300 nozzles and the resolution is 600 dpi; each nozzle discharges the ink drops of 35-85 pico-liter (pL) in volume. The printing system is based on a three-axis X-Y-θ table with micro-step resolution of 0.5μm up to 4 in/s speed, a set of printing heads, and an area CCD are fixed on the mechanical support. In operation, the firing distance between the substrate and the print head is adjusted at 500μm to get better printing quality. A waveform driving procedure is adopted to control the printing stability and quality. For more details, one can refer to Cheng et al.[14]

Measurement Tools

An optical-interferometry 3-D surface profiler was used to measure the thin film profile (SNU Precision Co., Korea). It had a vertical resolution of 0.1 nm, and lateral resolution of 0.5 μm. Scanning range can be adjusted from micro to nanometer, depending on the interferometric optics (2x-5x, Michelson interferometry, 10x-50x, Mirau interferometry). The contact angle of water on the self-assembled films was measured using an KRUSS drop shape analysis system (DSA 10 MK2). The surface morphology and surface roughness of dip and spin self-assembled multilayer films were investigated using the tapping mode of atomic force measurement (AFM Nanoscope).

Fabrication Processes

Before ink-jet printing of the catalyst material, a modification of surface property is required to increase the surface adhesion to the catalyst. In this work, we use the PEMs (Polyelectrolyte membranes) as our approach for the selective electroless plating of Cu. The membranes are contained PAH (Poly allylamine hydrochloride)/PAA (Poly acrylic acid) or PAH (Poly allylamine hydrochloride)/PSS (sodium styrenesulfonate) or hybrid polyelectrolytes (PAH/PSS/PAA). The key feature of PEMs based on PAH (Poly allylamine hydrochloride) and PAA (Poly acrylic acid) is the ability to alter multilayer surface functionalities with a single layer of polyelectrolyte, which can selectively bind with a Pd complex. A PAA-dominant surface binds a positively charged Pd complex, and then the catalyst is ink-jet printed onto the surface for patterning. And, finally, an electroless plating process was used to form the metal wire over the pattern of catalyst. All electroless chemicals are commercially available. It is worthy of mentioning, the printed substrate must immerse into Autotech Accelerator solution for 3~10 sec. This step can improve the catalytic ratio.

Results and Discussion

Surface Treatment of PAH/PSS/…/PAH/PAA

Commercial polyimide (PI) film is used to prepare substrate for layer-by-layer deposition. The film is rinsed with water and toluene, dried to constant temperature, and then storage at 40% relative humidity. Conditions for layer-by-layer deposition of poly (allylamine hydrochloride) (PAH) and poly (acrylic acid) (PAA) or poly (sodium styrenesulfonate) (PSS) are modeled by Decher. PAH is used as the polyelectrolyte for the first layer adsorption to PI film, PAA or PSS are the second layer and the covalently attached PAH layer to form the polyelectrolyte multilayer. The condition of adsorption PEMs layers can be monitored by the measurement of contact angle. Prior work reported the phenomenon[15,16] that the water contact angles measured climbed upwards with time on the PAH/PAA modified system. However, there is a significantly result on PAH/PSS modified system as indicated in Figure 1. Instead of showing the distinct periodic increasing with time, the water contact angle of PAH/PSS modified system is a constant value.

For ink jet printing process, it is appropriate range of surface contact angle from 30 degree to 70 degree. In addition, the surface uniformity of the polyelectrolyte membranes also plays an important role. The surface property of PAH/PAA modified membrane is varied with time, and made the line which is linked by ink jet printing be broken at higher contact angle (>70 degree) or diffused at lower it (<30 degree). However, the PAH/PSS modified system membrane can provide a uniformity and stable surface (water contact angle almost is equal to 40 degree). Hence, the PAH/PSS layer structure can be utilized as a perfect film modified on the substrate.

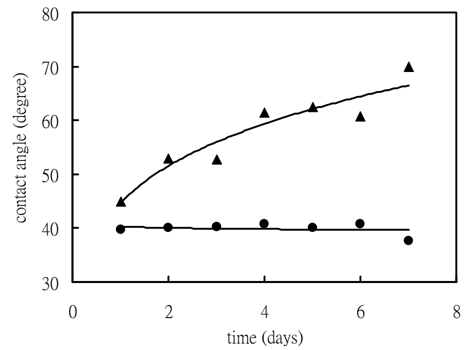

Figure 1. Film stability changes with time. After printing of the catalyst, the substrate was first baked in oven at 40℃ for 30 minutes, and then stored at 40% relative humidity for days. (▲: PAH/PAA modified system; ●: PAH/PAA modified system)

Rubner et al. demonstrated that ink jet printing has been successfully used to pattern PEMs. In his process, Pd-complex binds to the free carboxylic acid group of PAA and forms the Pd nanoparticles. These particles catalyze the electroless metal plating reaction and form electric circuits. Unfortunately, although PSS surface has better properties, but has no COOH functional group, so it never exchanges for protons and form Pd nanoparticles by reduce reaction. Therefore we describe a novel hybrid multilayer model. This membrane combined PAA/PAH and PSS/PAH regions. The inner layers, PAH/PSS layers, were supplied an uniform and higher contact angle porous film. The outmost layer, PAA/PAH layer, could provide available surface to react with Pd-complex, which is printed by Ink-Jet as indicated in Figure 2. The result of contact angle on this hybrid multilayer film is about 40 degree. This result is conformed to previous studies, the properties of surface are related to bulk PAH/PSS multilayer and irrelevant to only the outmost PAH/PAA bilayer.

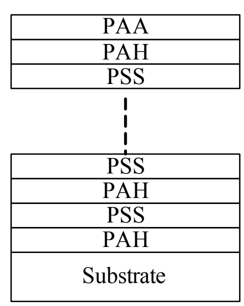

Figure 2. Layer structure of hybrid polyelectrolyte multilayer layers deposited on substrate.

Surface Analysis

To further analyze the detail of multilayer, Fig3. shown the atomic force microscopy (AFM) images depicting the surface topography of the (a) PAH/PAA multilayer (7 double layers, the outermost layer is PAH), (b) PAH/PSS multilayer (7 double layers, the outermost layer is PSS), (c) hybrid multilayer (combines 6 double PAH/PSS multilayer and 1 double layer, the outermost layer is PAA), and (d) on the PI substrate. In Fig. 3(a), the original maximum roughness of PAH/PAA multilayer sample is about 40 nm, and a porous structure is formed with high surface area as shown in it. The 3μm × 3μm scans showed the multilayer film forming high-density of small grains approximately 50-250 nm in size. It is suspected that the larger grain size of nearly 250 μm is either contaminated by particles or the primitive property of substrate, same as observed in Fig. 9. The surface RMS (root-mean-square) roughness on PAH/PSS multilayer and hybrid multilayer are about 3.2 nm and 3.4 nm as observed in Fig. 9(b) and Fig. 9(c), respectively. This result is identical with previous reports. In general, the roughness of strong polyelectrolyte like PAH/PSS multilayer is always thinner than weak poly-electrolyte like PAH/PAA multilayer in the same number of layers. Therefore, as presented in Fig. 3 (d), after printing of the Pd-complex catalyst, subsequent reduction by hydrogen, forms zero-valent Pd nanoparticles within the multilayer. When Cu replaced Pd by the reduction reaction in the electroless plating, the copper is deposited near the root. This resulted in excellent adhesion property between Cu and the substrate.

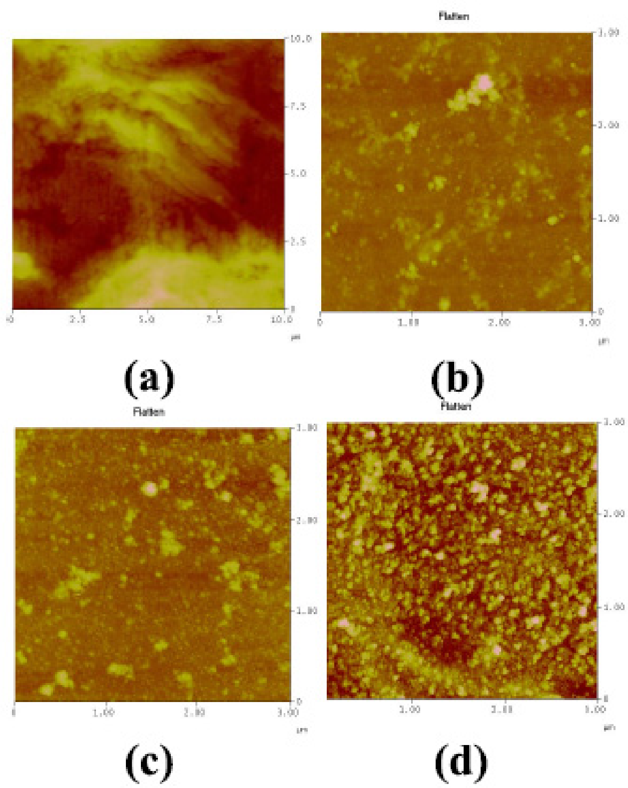

Figure 3. AFM tapping mode images of (a) the surface of seven PAH/PAA double layers/ Polyimide substrate, where PAH is the outermost layer; (b) the surface of seven PAH/PSS double layers /Polyimide substrate, where PSS is the outermost layer; (c) the surface of seven PAH/PAA double layers and one PAH/PAA layer /Polyimide substrate, where PAA is the outermost layer; (d) Pd catalyst adsorbed on the surface of a printed PAA surface on seven PAH/PAA double layers and one PAH/PAA layer /Polyimide substrate, where PAA is the outermost layer.

Ink Jet Process

Rubner et al. demonstrated that ink jet printing using to pattern PEMs deposited by dipping. However, the next generation processes bring benefits of avoiding the substrate deformation in dipping step, especially for paper substrate in RFID (Radio Frequency Identification) application. Therefore, we attempt to accomplish all the processes include the layer-by-layer polyelectrolyte multilayers, and the catalyst layer is patterned by all ink-jet method. The preliminary experiment result is confirmed that the feasibility of this process which all ink-jet process. As presented in Fig. 4(a) and Fig. 4(b), AFM images depicting the surface topography of the hybrid multilayer (combines 6 double PAH/PSS multilayer by ink-jet printing and 1 double layer, the outermost layer is PAA by ink-jet printing). The surface morphology is similar with same PEM constructed by dipping. However, the surface RMS (root-mean-square) roughness on this surface is about 3.8 nm and slightly rougher than same PEM structure. To our knowledge, this is the first time that inkjet printing has been successfully used to accomplish all the processes include the layer by layer polyelectrolyte multilayers, and the catalyst layer.

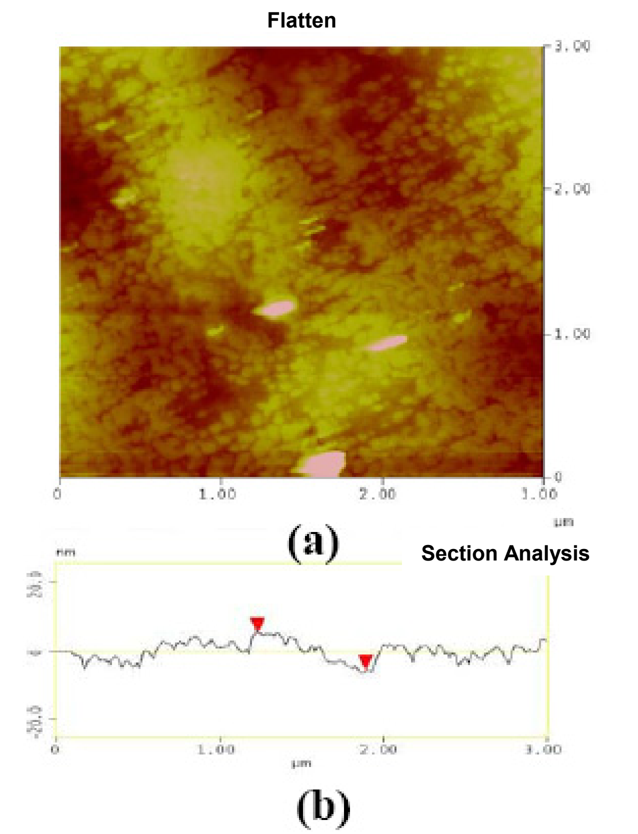

Figure 4. (a) AFM tapping mode images of the hybrid multilayer (combines 6 double PAH/PSS multilayer and 1 double layer, the outermost layer is PAA). (b) The roughness profile images of it.

Electroless Plating Process

An optical image of a typical substrate after electroless deposition process is shown in Figure 5. The metal regions are where the jetted Pd-complex to form catalytic line and copper then deposited. These showed a typical metal line width about 80μm and 75μm on PI and FR-4 substrate, as presented in Fig. 5(a) and 5(b). This specific result is related to the roughness ratio of substrate. In the Fig. 5(c), metal line is fabricated by electroless plating process and its patterning and surface treatment are accomplished by all ink jet method. In addition, the growth rate of thickness is related to time, it is about 6μm per hours. And the resistance will dramatic decrease with the plating time. The best condition is about two times of bulk resistivity of copper ($\rho_{bulk,\,cu}$ = 1.67μΩ.cm).

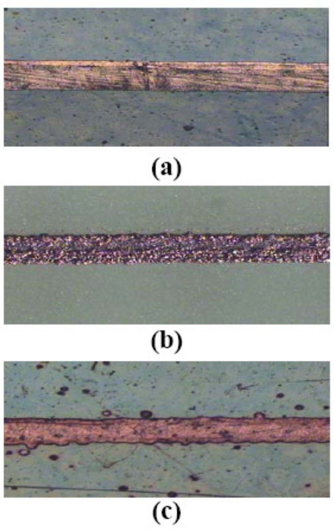

Figure 5. Cu metal line forming by ink-jet catalyst and electroless plating on the different substrate modified with hybrid PEM (a) PI substrate and (b) FR-4 substrate). The average line width is about 80μm and 75 μm. (c) metal line is fabricated by electroless plating process and its patterning and surface treatment are accomplished by all ink jet.

Conclusion

In this paper, a fabrication process of specific membrane that consists of two kinds of polyelectrolytes adsorption was successfully verification. This hybrid membrane combined PAA/PAH and PSS/PAH layers. The inner layers, PAH/PSS layers, were supplied a uniform and higher contact angle porous film. The outmost layer, PAA/PAH layer, could provide available surface to react with Pd-complex, which is printed by ink-jet. We found high performance metal circuits after printing and electroless deposition by these treatment processes,. In addition, ink-jet method process has been demonstrated primarily, including layer-by-layer PEM and micro-disposed catalyst. These processes bring benefits of avoiding the substrate deformation in dipping step, especially for paper substrate in RFID (Radio Frequency Identification) application.

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