Method for Forming Cu Metal Wires by Microdispensing Pattern, Part I:

Self Assembly Treatment & The Ink-Jet Process

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Abstract

In this paper, we successfully combined three processes: self-assembled polyelectrolytes, catalyst ink-jet printing, and electroless metal plating technologies for the fabrication of electronic circuits. Poly (acrylic acid) (PAA) and poly (allylamine hydrochloride) (PAH) are primarily layer-by-layer adsorbed on the substrate. An inkjet-deposuted catalyst pattern binds by ion exchange to topped-surface PAH and forms metal nanoparticles. Finally, the electroless plating process form the electronic circuit on the pattern of catalyst. Besides, the process of immersing in acidic aqueous environments causes the microporous transformation. Therefore, due to the higher surface area and the microporous structure, these self-assembled polyelectrolyte layers are of great benefit to the absorption of the catalyst used for metal deposition. Hence, the above processes form excellent metal pattern for various substrate, like PET, Glass, PI, FR-4 etc.

Introduction

Electroless plating of metal, particularly copper or nickel, is an important industrial technique for metallizing on plastics substrate and objects with geometries that are difficult to coat by electroplating. One important example is the use of electroless copper and nickel in printed circuit boards to form interconnects. In contrast to electroplating, where an applied current supplies electrons to reduce a high-oxidation-state metal precursor, the basis of electroless plating is an autocatalytic redox reaction. The important material prerequisite for initiating metal deposition is the presence of an appropriate catalytic surface.

Classical PCB processes include the step of attaching dry metal film to substrate, spining photo resist, masking pattern & 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. These techniques have served the industry well and provided the desired image resolution at an acceptable cost. Both methods have their own individual strengths and weaknesses and manufacturers select the most appropriate process for their requirements in primary track imaging, solder mask application and legend printing. These methods suffer from the drawback of being analogue processes and hence require conversion from a digital data file to printable image via initial production of a screen or photo tool. This adds cost and time delays to the preparation of boards, particularly for prototype and short run board production.

IJ technology has grown from an academic curiosity to a major force in printing over the last 25 years and many excellent reviews describing the fundamental principals and head technology have been published. It has been widely adopted in many printing, patterning and related processes for three principal reasons. First, it is a direct method to accurately place material in one step. And secondly, it is a digital process and thus affords the ability to write data and continuously change the output, without the need of any intermediate stages. Thirdly, it provides a non-impact method to deposit significant quantities of materials to provide an end effect. These properties make IJ ideally set up for introduction in to PCB manufacturing processes

In this paper, an unique approach combining self-assembled polyelectrolytes, ink-jet printing, and electroless metal plating technologies for fabrication of electrical circuits was development.

Experimental Apparatus

We have developed an ink jet system with a special designed thermal ink jet head for patterning. During the printing process, ink-jet heads scan relative to the substrate while discharging inks into patterned bank area, and a waveform driving procedure is adopted to control the printing stability and quality[1]. The system details can refer Cheng et al.[2] For inspection, an optical -interferometry surface profiler is used to measure the thin film profile (SNU Presision Co.).

Experimental Procedure

In classical process, the circuit board is immersed in a solution containing a Pd/Sn colloidal suspension. The surface of circuit board is often pretreated to promote the

adhesion of the metal colloid. After the absorption of the metal colloid, the surface is coated with a photoresist and developed to reveal the circuit pattern. Copper is grown on the exposed circuit pattern by placing the circuit board in a copper sulfate bath containing formaldehyde.[3] where the copper reduction is catalyzed by the exposed metal colloid. The typical copper line delineated is ~100 μm.[4] In this paper, it presents an alternative approach to form metal circuit lines on a substrate pretreated by self-assembly steps, and then employs the direct printing of the catalyst, which is used for the electroless plating operation. This method is versatile and inexpensive, produces highly conductive metal lines less than 100μm wide, and the thickness can control from sub-microns to about 35 μm.

Before ink-jet printing of catalyst material, it needs appropriatly modify the surface properties of substrate, to increase the adhesion between the interface. Here we use the PEMs as a platform for the selective electroless plating of metal. Key features of PEMs based on PAH (Poly(allylamine hydrochloride)) and PAA (Poly(acrylic acid)) with the ability to alter multilayer surface functionalities with a single layer of polyelectrolyte, surfaces that selective bind with catalyst can be prepared. A PAA-dominant surface binds a positively charged catalyst, while a PAH-dominant surface resists binding. With a negatively charged catalyst, the PAH-dominant surface binds the catalyst, while a PAA-dominant surface resists binding. Electroless plating is selectively promoted only on the PAA or PAH surface and inhibited on the other with only one polyelectrolyte layer difference. The PAH / PAA multilayer contains region of PAA or PAH outermost layers are used to direct plating only to the PAA or PAH surfaces. In this invention, the PEMs processes modified the substrate surface, and an ink-jet printing of catalyst materials onto this surface to get patterned catalyst distribution, and finally an electroless plating process to form the metal wire on the pattern of catalyst.

Self-Assembly Step

Self-assembling monolayer (SAM) films have been used as building units for constructing multilayer structures and as modifiers of surface properties. Such surface modification, for example, can be used to promote adhesion and wettability, prevent corrosion, modify the electrical and optical properties of the material or create electroactive monolayers suitable for various optical and electronic sensors and devices.[5-9] SAMs are prepared by selective absorption of compounds at solid fluid interfaces to construct organized oriented compact monolayers of good quality and having a thickness ranging from about 1 nanometer to about 3 nanometers. The molecular self-assembly process takes place as a layer-to-layer process, which is based on the spontaneous absorption of either nonionic polymers, polyanions or polycations from dilute aqueous solutions onto surfaces that carry a functional group or a charge opposite to that of the depositing polymer. Selective absorption of these polyelectrolytes is alternated to form a bilayer assembly and leads to the formation of multilayer assemblies. The molecules are typically used for constructing the first monolayer have a terminal polar group and a non-polar functional group at either the other end of the molecule or somewhere within it.

The chemicals are prepared as description below. The need of chemicals are PAH, sodium tetrachloropalladate, PAA, dimethylamine borane, soldium citrate and lactic acid were obtained. All chemicals were used without further purification. Deionized water was exclusively used in all aqueous solutions and rinsing procedures. The PAA and PAH solution were maintained in certain pH range, which was tuned by HCl and NaOH solutions as Wang et al. suggested procedure.[10] The catalyst solution to enable the metal ions to be absorbed with PAH due to the interaction between the metal ions and ammonium groups of PAH. The sodium tetrachloropalladate was dissolved in di-water as the catalyst solution. The copper electroless plating solution has two formulas in this study, but it has only little difference appearance in growing rate, the recipe b was preferred all this study for its easy prepared.

PAH/PAA – based multi-layers were fabricated on glass substrate, PET substrate or FR-4 substrate. PAH aqueous solution was adjusted to near neutral, and PAA aqueous solution was adjusted to acidity with HCl. Other pH conditions were similarly obtained by adding the appropriate amount of acid or base. The pH value determines the fraction of functional groups that will be ionized during the assembly process; it is possible to control the density of non-ionic, reactive functional groups. Generally, the pH value will control at the completed ionized for PAA and PAH to get well stoichoimetric pairing. In this study, multi-layers were formed by first immersed substrates into the PAH solution several minutes followed by immersing into water as rinsing steps. The substrates then were immersed into the PAA solution for several minutes followed by identical rinsing steps. The absorption and rinsing steps were repeated until the desired number of bi-layers was obtained. One bi-layer is defined operationally as a single absorption of PAH followed by absorption of PAA. The PEM was finally dried in air and stored under ambient conditions. The HCl dipping step is a treatment on the PAA/PAH bi-layers structure, Rubner[11] found the step control the transformation of a dense multilayer film to a microporous multilayer film. For this application, it dominates the interface between catalyst and the PAA/PAH bi-layer, and indeed determines the adhesion property of metal after electroless plating.

Past patterning techniques using thin films as only passive resists have not provided patterned SAMs with uniform patterns or the high resolution required for potential applications such as full color flat displays, electroluminescent devices, conducting and insulating circuits, optical and nonlinear optical devices, and multi-element chemical sensors. Therefore, it is desirable to prepare uniform and consistently patterned SAMs, which may be used to fabricate such devices. In this study, the pattern step is realized by ink-jet printing of catalyst on the self-assembly multi-layers structure, and forms the metal wire by typical electroless plating technique. It is a modified approach with previous study of Guo et al.[10] In previous

study, Guo et al. operated ink-jet printing the PAH solution as the patterning step, and then immersed the substrate into the catalyst solution. Their procedure needs careful control the DI-water flushing step and electroless plating time, to avoid low selection on the substrate because of some remainder of PAA layer will absorb catalyst during immersing process. Longer immersing time will make metal deposition on the back side of substrate in sunsequent electroless plating step, and shorter immersing time will get deterioration at metal line uniformity. Figure1(a)-(e) compared the difference and showed the results.

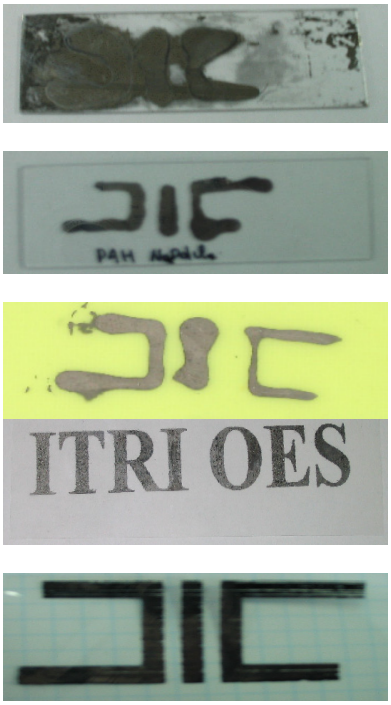

Figure 1(a)-(e). Comparison of ink-jet patterning for different ink solution. All procedures and testing conditions follow Guo et al. report.[10] Three PEMs layer has been on substrate. (a) Drawing outmost PAH pattern on glass substrate, and dipping the glass substrate into catalyst solution, it showed bad selection of Ni, and Ni deposition in backside of glass substrate. (b) Dipping a layer of PAH on glass substrate, and then drawing a catalyst solution pattern on glass substrate. It showed excellent selection of Ni, and no Ni deposition in backside of glass substrate. (c) Dipping a layer of PAH on FR-4 substrate, and then drawing catalyst solution pattern on FR-4 substrate. It showed excellent selection of Ni, and no Ni deposition in backside of FR-4 substrate. (d) Dipping a layer of PAH on PET substrate, and then ink-jet printing catalyst solution on PET substrate. It showed excellent selection of Ni, and no Ni deposition in backside of PET substrate. (e) Dipping a layer of PAH on PET substrate, and then ink-jet printing catalyst solution on PET substrate. It showed excellent selection of Cu, and no Cu deposition in backside of PET substrate.

Ink-Jet Printing Step:

A commercial ink-jet printer was filled with catalyst in DI water. Printing can be done primarily on polyethylene terephthalate sheets, FR-4 substrate or glass 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.

Electroless Copper Plating Step

The copper plating bath was based on the general formulation.[12] 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 room temperature. 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.

Results

The electroless plating controlled the thickness of the metal film formation. The key factors are the plating bath concentration, the temperature, the pH stability, the additives, and the plating time. For this study, we didn't focus on the interaction between these factors, for previous researchers have many studies on their relation. During the plating process, we keep the same concentration of plating bath at fixed temperature and pH value, and growth the metal thickness by control the plating time. Shiratori[13] pointed out the surface roughness can influence the thickness of an absorbed monolayer, with thicker layers being formed on multi-layers of high roughness. In this study, the substrate FR-4 has primitive roughness about 2 μm before SAMs layers processing

Figure 2 defined the image pattern for printing the catalyst. L1-L6 arelines of different width. The thinnest is L1 with line width of 75μm and it increases 25 μm for each line, up to L6 of 200 μm. P1-P7 means for the measurement points, each point has a square pad to contact the probe.

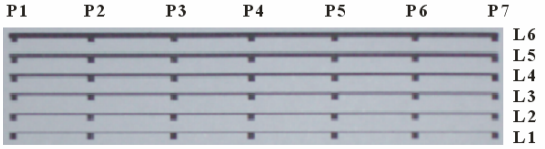

Figure 2. Measurement point and test pattern for printing catalyst. L: Line. P: Point. Original line pattern is start at width of 75μm for L1, and increases 25μm each line up to L6.

Figure 3 showed the curve of plating time vs. metal thickness, and it indicated a linear relation at operation within about 180 min. Over 180 min, we found the line profile near mushroom, and it made the non-linear behavior in Fig. 3. The linear average growth rate was estimated about 16 μm /150 min, near 0.1 μm / min deposition rate. Figure 4 showed a typical metal line width about 92 μm with printing catalyst line L1 (75μm). Observed by optical magnification, one can find that the line surface was not uniform because the different light scattering, and the line has blurring edge caused by print head drop instability. It is notable when the ink drop lands on the substrate, the spreading factor caused by surface property will make the droplet flow, and it showed a wider line width than original image pattern define. Another factor made the wider line than original image pattern was the hetero-isotropy growth in electroless plating, but the later is not discussed in this study.

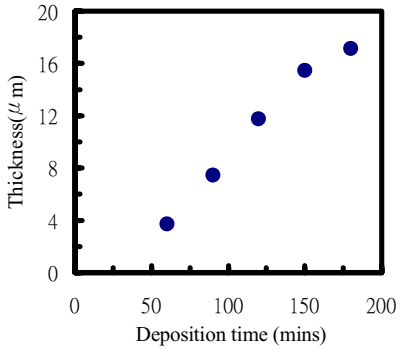

Figure 3. Electroless plating stability curve of deposition time vs. metal thickness.

Figure 4. Cu metal line forming by ink-jet catalyst and electroless plating. The average line width is about 92μm.

Figure 5 was the measured data for printing catalyst line L1-L6 between P1-P2 for different plating time. As described in Fig. 5, the results presented that the resistance will dramatic decrease with the plating time, and it indicated that the resistance keep linear relation with the measurement distance. Figure 6 indicated that the resistance varies inversely with the line width. A typical example for plating time over 60 minutes, the L2 has thickness about 4μm, its resistance less than 10Ω/10 cm. The best condition of L1-L6 has the resistance about 0.304Ω/cm, at the metal line width 250μm and line thickness 17μm. It is about eight times of bulk resistivity of copper ($\rho_{bulk,\,cu}$ = 1.67μΩ.cm).

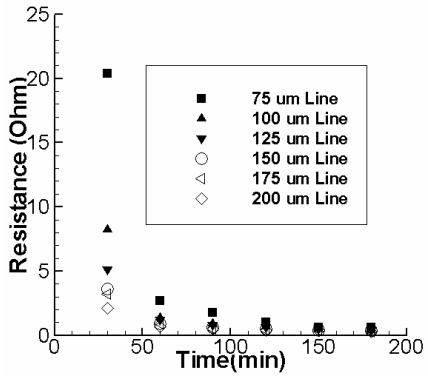

Figure 5. Resistance varies with different line width and electroless plating time. The measure point is the P1-P2 in Fig. 5, for L1-L6. L1-L6: 75μm, 100μm, 125μm, 150μm, 175μm, 200μm line width of test pattern for printing catalyst.

Conclusion

A patterned molecular self-assembly is provided to use for forming conducting wire. The patterned molecular self-assembly comprises a step of self-assembly layers on substrate, a step of micro-dispensing catalyst on the said self-assembly, and a step of forming conducting wire by electroless processes. The patterned molecular self-assembly comprise at least a set of bi-layers, and can further comprise bi-layers structure layer-by-layer.

In this invention, it presents an alternative approach to forming metal circuit lines on a substrate pretreated by self-assembly, and direct printing of the catalyst, which is used for the electroless plating operation. This method is versatile and inexpensive, and produces highly conductive metal lines less than 100μm wide with thickness ranging from submicron to about 35um.

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Biography

Ming-Huan Yang received his Master degree in Chemistry from National Cheng Kung University in 2002. He is now a system integration engineer in the Printing Technology Division, Opto-Electronics and Systems Laboratories of Industrial Technology Research Institute at Taiwan. His work has primarily focused on the industrial ink-jet printing processes development, especially in PCB fabrication by ink-jet printing. E-Mail : miltenyang@itri.org.tw