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Nanoinks in inkjet metallization — Evolution of simple additive-type metal patterning

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ABSTRACT

Recent advances in the development of stable dispersions of nanophase metal particles have allowed the direct fabrication of metal patterns (e.g., printed circuits, RFID tags, touch screens, etc.) by simple additive type inkjet processes. Such processes replace the more costly and less environmentally friendly subtractive lithographic type photoprocesses involving selective etching of photoresists and metal layers and more complex additive type process using photocatalysts for patterned metal deposition by electroless plating processes and inkjet patterning of metal catalyst or catalyst precursor for subsequent metallization by electroless plating. The recent development of electrohydrodynamic jet printing (e-jet printing), in which the ink drop is ejected under the influence of an electric field, has allowed a significant resolution increase vs. conventional inkjet printing with a piezoelectric head (printing resolution of ca. 100 nm for e-jet printing vs. ca. 20 μm for inkjet printing).

1. The evolution of solution metal deposition processes — subtractive to additive

The synthesis of stable nanophase metal dispersions [1–5], coupled with the development of ink jet printing technology [6–11], and, more recently, electrohydrodynamic jet (e-jet) printing [13–23] has led to the development of convenient new fabrication processes for printed circuits and related conductive metal patterns by inkjet processes [24–26*]. These additive type processes provide a significant advantage over the earlier subtractive type processes. The conventional fabrication of printed circuits uses a multistep photolithographic subtractive type process involving several chemical steps — e.g., coat a metal layer, typically copper, with a photoresist, imagewise expose the photoresist layer through a mask to provide a solubility difference in the exposed and unexposed areas of the photopolymer (both positive and negative working photoresists are known), solvent etch the photopolymer to selectively expose the underlying metal layer, and finally solvent etch the exposed metal layer to provide the desired printed circuit [27–31]. In addition to the time-consuming nature of such processes, the disposal of the etched materials also imposes a significant process cost due to environmental regulations. A metal patterning process with only one etch used the following steps [32]:

- deposit a layer of photoresist on a substrate
- form a pattern on the photoresist by light exposure through a mask
- deposit a layer of metal nanoparticles on the patterned photoresist
- remove the photoresist and overlying metal nanoparticles on the photoresist
- sinter the remaining nanoparticles to form a metallic pattern.

Another lithographic one-etch process [33] provides the direct ultraviolet (UV) imprinting of silver patterns using an acrylate-based resin incorporating a nano-silver colloid, with post-imprinting steps involving heat treatment to sinter the nanosilver particles and wet etching. The electrical resistivity for 60 wt.% Ag loading was roughly 2.5 times higher than that of bulk silver.

A second generation technology for printed circuits provides an additive process but also has severe chemical restrictions. In such processes a photocatalyst, typically a Pd(2+) compound, is uniformly coated on a suitable substrate, imagewise exposed to appropriate radiation (through a mask or using laser writing) to generate a pattern of metal catalyst, and the printed circuit is then generated by treatment of the imaged substrate with an electroless plating solution [34–39]. These solutions, comprising a metal ion, a complexing agent and a reducing agent (the commercial plating solutions generally also incorporate other addenda to promote the formation of bright metal deposits, etc.) are thermodynamically unstable with respect to metal deposition but kinetically stable for some period of time (minutes to days, depending on the particular combination of the three main

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components) [40–43]. A wide variety of such metal electroless plating solutions are known in the literature, as well as being commercially available (e.g., Cu [44–50], Ni [51–57] (the Ni deposited from these plating solutions can incorporate P and B from the reducing agent (e.g., NaH_2PO_2 [51] or amine boranes (e.g., dimethylamine borane ($Me_2(H)NBH_3$) [52]) used in the plating baths), Ag [58–61], Au [62–66], Pd [67–71], Pt [72–74], Co [75–77], Rh [78–80], Sn [81–83]). Commercial electroless plating solutions are typically supplied as two solutions which are mixed just prior to use (1 — metal compound and complexing agent and 2 — reducing agent). The most common systems of this type use palladium(2+) complexes as the photoelement, since Pd(0) is an excellent catalyst for a wide variety of electroless plating solutions, and Pd(2+) compounds readily undergo photoreduction to give the active Pd(0) catalyst for metal deposition from the metal plating solution. An example of such an additive system for fabrication of printed circuits on a flexible support is a polyethyleneterphthalate film (Estar® [84]) coated with potassium palladium oxalate, $K_2[Pd(C_2O_4)_2]$, [34] in a thin cross-linked gelatin layer on this film base. The thin surface gelatin layer, which is water insoluble but water permeable allowing penetration of the aqueous plating solution, also provides Pd(2+) binding sites for the photocatalyst which is coated onto the film from an aqueous solution. Surface modification of polymeric substrates such as the polyimide Kapton® [85] and polyethyleneterphthalate (PET) (Kodak Estar® [84]; DuPont Mylar® [86]) by chemical treatment [87,88], plasma or corona discharge [89–95] to provide binding sites for Pd(2+) have also been reported. Although these additive type systems eliminate the need for disposal of etched photoresist and metal, they require very careful selection of reducing agent in the plating solution to avoid spontaneous reduction of Pd(2+) in the background area (i.e., the areas not exposed to radiation to effect the Pd(2+) to Pd(0) photoreduction) which would give unwanted metallization [34]. In addition, the use of electroless plating solutions in the final metallization step requires careful control of the process conditions (reagent concentrations, temperature and pH). These processes, however, require no thermal annealing treatment after the metal deposition as is generally the case for metal patterns deposited by inkjet processes using nanophase metal inks [24–26•].

A third generation process eliminated the uniform photocatalyst layer by inkjet addressing the substrate with an ink comprising an aqueous dispersion of catalytic metal nanoparticles [96] or metal catalyst precursor compounds [97], with electroless plating used to generate the final metal pattern. This process eliminates the problem of background metallization by unwanted reduction of a uniform photocatalyst layer [34] but still requires the use of an electroless plating solution for the final step of the metallization.

The ultimate solution to selective solution metallization has now been achieved, and commercialized — the use of inks comprising dispersions of nanophase metals to directly provide, after suitable thermal processing, the final metal pattern [24–26•]. Such processes eliminate the need for separate steps for catalyst patterning (by patterned photoreduction of metal catalyst precursor [34] or inkjet delivery of a metal catalyst [96] or catalyst precursor [97]) and final metallization with electroless plating solutions associated with the earlier additive type processes. The critical material science components of these new direct metallization processes are: 1. — inks comprising stable dispersion of the nanometals and 2. — suitable surface modification and thermal stability of the substrate to provide the required adhesion of the inkjet delivered nanometal and final thermal processing to provide the desired metal conductivity. Current commercial inkjet technology can pattern relatively large areas on a resolution scale of 100 μm. Large-format commercial printers commonly range up to 4 ft. in print width, and industrial high-throughput printers can accommodate textiles in 96 in. formats or greater.

The most recent refinement of inkjet metallization is electrohydrodynamic jet (e-jet) printing technology [12–23] which delivers the ink drops under the influence of an electric field and can provide a significant increase in resolution of the metal patterns compared to conventional inkjet printing — e.g., resolutions of ca. 100 nm vs. ca. 20 μm for inkjet printing. The concentration of ions allows the tip of the cone to break away and form droplets that are just a fraction of the volume of the cone. The use of e-jet printers, that currently can precisely print dots of various materials 250 nm in diameter, offers the possibility to rapidly fabricate complex nanoscale structures out of various materials.

Recent work by the Rogers group at the University of Illinois [19], for example, demonstrated e-jet printing that can pattern large areas with block-copolymers based on poly(styrene-block-methylmethacrylate) to give geometries with diameters and linewidths in the sub-500 nm range, line edge roughness as small as ~45 nm, and thickness uniformity and repeatability that can approach molecular length scales (~2 nm).

This review provides an overview of the evolution of patterned metallization processes over the past 30 years, from the early chemically complex subtractive photolithographic methods [27–31] to the current processes using commercial nanometal inks for the totally additive fabrication of metal patterns and interconnects in applications such as printed circuits, RFID antennas, touch screens, solar cells, thin film transistors, electroluminescent devices and OLED displays. An excellent comprehensive journal review of inkjet metallization processes has also been recently published [26•].

2. Fabrication of metal patterns by ink jet delivery of metal catalyst precursor or metal catalyst nanoparticles followed by electroless plating

The three key enabling technologies for the development of inkjet metallization processes have been the development of synthetic methodology for metal nanoparticles (inorganic synthesis) and stable dispersions of these materials (colloid chemistry) [1] and substrate surface modification to provide good adhesion of the metal to the substrate, often a polymer film for flexible electronics [87–95]. Surface modification of polymeric films for use as flexible substrates in inkjet metallization processes (and coatable electronics, in general) includes the coating of a thin film of a second functional polymer on the film base. Gel-subbed Estar® (polyethyleneterphthalate, PET), available from Eastman Kodak Co., for example, has a thin layer of cross-linked gelatin on the surface that provides binding sites for metal ions such as Pd(2+) [34,84]. PET is also available from DuPont as Mylar® [86]. Chemical etching [87,88] and surface plasma treatments [89–95] have been widely used to give surfaces that provide binding sites for metallization catalysts as well as good adhesion of metal coatings. Since thermal annealing is generally used to process inkjet deposited metal nanoparticles (to eliminate surface stabilizing agents, allow aggregation of the metal nanoparticles and provide high conductivity [26•]), the thermal stability of the polymeric film base is also critical — e.g., PET can be used up to ca. 120 °C and Kapton®, a DuPont polyimide [85] can be used up to ca. 150 °C.

Two and three step modifications of inkjet metallization involving final metallization by electroless plating catalyzed by an inkjet-patterned catalyst include the following variations:

1. inkjet delivery of metallization catalyst followed by electroless plating of the final metal pattern (immersion of the substrate with inkjet patterned catalyst into an electroless plating bath) [96];
2. inkjet delivery of a metallization catalyst precursor followed by electroless plating metallization (immersion of the substrate with an inkjet patterned catalyst precursor, e.g., Pd(2+), into the electroless plating bath with the patterned catalyst precursor being initially reduced to the active metallic catalyst by the reducing agent of the electroless plating bath) [97];
3. inkjet delivery of metallization catalyst and 2 components of the electroless plating bath.