Deposition of Thin Copper in Pre-formed Vias on Thin Flexible Base Materials

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Abstract
This paper reports on further developments for an innovative copper deposition technology that was presented two years ago at this conference. At that time, the innovative technology was described as a way to replace conventional sputtering and vacuum deposition techniques while achieving greater feature diversity, lower cost, and higher performance. The advancements reported here include the extension of the technology to deposit thin (depths of 0.1 to 10.0 microns) copper with good adhesion on the interior of via walls that have been pre-formed in the base material. This process extension has been demonstrated on vias as small as 25 microns in diameter and on thin (7.5 to 12.5 micron) polyimide base materials.

The Need: Flexible Printed Circuit Boards
Printed circuit boards were invented many decades ago to replace the discrete wires that were used to connect discrete electrical and electronic components in electronic equipment. As electronic components became smaller and more integrated, the physical requirements for printed circuit changed as well. Originally printed circuit boards had to be rigid and large with thick copper conducting paths to handle the relatively high current and weight of the devices. With the advent of small, integrated, low power, high frequency components, the requirements for printed circuit boards trended toward thinner copper, thinner and flexible substrates, narrower lines, and closer lines to promote dense packing. Thus over the last two decades, thin copper, dense packing, and, of course, lower cost have been the key priorities for the development of flexible circuit materials and the processes used to manufacture flexible circuit boards.

The market for flex circuits today is over $10 billion per year and is being driven by the needs of new high performance consumer electronics (e.g. cell phones, laptops, etc.) as well as by medical and military applications. These applications are approaching the limits of the durability, speed, and bandwidth of the conventional subtractive etch processes used today to make flex circuits. Product designers want to pack more electronics in smaller spaces which means greater circuit density is required. Circuit density usually means more circuit complexity and more layers. Also since flex circuit manufacturing and warranty costs are proportional to the square of the number of layers, the cost of new product designs using existing manufacturing methods are increasing exponentially. Solving this “three dimensional” problem requires narrower and more closely spaced conductors, thinner layers of conductor metal, elimination of tie coat materials, and lower cost manufacturing. And ideally, the solution should also use greener manufacturing processes. The innovative print and plate technology described herein can provide all these benefits.

Another growing need is for more ecologically friendly processes and materials. For flex circuits this means minimization of the waste of materials and minimization of the use of environmentally toxic or unfriendly materials. Subtractive etch processes use a variety of etchant solutions to remove between 50% to 75% of the original metal from the flex circuit material. Semi-additive vacuum sputtered metal processes typically use a seed layer of chromium which is a heavy metal that is being removed from the market by new environmental regulations in the North American and European markets and which also requires an etchant process.

Another need is for greater physical reliability. As flex circuits get thinner, denser, and implemented in more demanding applications, the reliability and lifetime become more important. A typical failure mode for flex circuits that have to undergo either a high number of flexes or very acute angle flexes is the delaminating of the copper circuit from the substrate.

Competing Technical Approaches
The prevailing method for manufacturing flexible circuit boards is to begin with a flexible high dielectric substrate material such as polyimide which has a layer of copper covering the entirety of one or both sides. From this “flex circuit material”, circuit lines and pads can be etched and holes or vias drilled to provide the finished flexible board to which components can then be affixed.

The prevailing method for attaching layers of copper to polyimide is gluing a foil of copper using an adhesive to the substrate using a lamination like technique. However, as thinner copper layers and thinner substrates are required, relatively thick layers of adhesive become less practical and often a source of delamination failure. Thus techniques for depositing copper on flexible plastic substrates that do not require adhesives and promise improved reliability and lower cost are in need.

In addition to the different forms of flex circuit materials, there are several methods for creating the circuits from the materials. These can be categorized as (1) subtractive, (2) semi-additive, and (3) additive.

A subtractive process starts with a flex circuit material that has a layer of copper that totally covers the surface of a substrate. For positive resists, the resist is exposed with UV light wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist so that it becomes more soluble in the developer. The exposed resist is then washed away by the developer solution, leaving windows of the bare underlying material. In other words, "whatever shows, goes." The mask, therefore, contains an exact copy of the pattern which is to remain on the wafer.

Typically then a photolithographic process using a positive resist material and UV light is used to image the circuitry that is to be formed from the copper layer on the substrate. The resist is exposed with UV light shining through a metal mask. In these resists, exposure to the UV light changes the chemical structure of the resist so that it becomes more soluble in the developer. The exposed resist is then washed away by the developer solution, leaving copper exposed. The mask, therefore, contains an exact copy of the copper pattern which is to remain on the substrate. After the photo resist material is washed away, the copper that is not covered by the mask has to be removed using an etchant solution to leave behind the copper that represents the circuitry with the resist material still covering it. The remaining resist material then has to be dissolved to complete the circuit formation process. The vast majority of processes used today to make flex circuitry are subtractive in nature.

A semi-additive process implies that some of the steps in the circuit formation process are additive and some are subtractive. Typically, a semi-additive process features a thin “seed” layer of a conductive metal such as copper that covers the entire surface of the substrate. A negative mask of the circuitry to be created is then deposited on the seed layer. Because the seed layer is conductive, an electroplating process can then be used to build up copper to the desired thickness in the areas uncovered by the mask. The mask and the seed layer of copper under the mask are then etched away thusly leaving the desired metal circuit patterns and exposed non-conductive substrate.

An additive process implies that copper is deposited directly in the desired pattern and that no etching or material removal is required to complete the circuitry. If this can be accomplished in high volume and low cost, this is an ideal approach for flex circuit production. There are few processes commercially available today that are purely additive although there is considerable research ongoing to perfect a variety of copper “printing” techniques. To date these have been based on a printing technology that deposits a conducting ink on a substrate. While there are advantages of printing directly with conducting ink, there are severe limitations in the performance, reliability, and lifetime of circuits made with these techniques. Conducting inks are usually a mixture of UV or thermal curable liquid polymers and conducting metal particles. In these inks, adhesion is achieved primarily because the ink itself is an adhesive material that is conducting when dried because of the physical contact of some portion of the conducting particles or flakes that were mixed into the liquid. The conductance and durability of these conducting inks are lower than pure metal circuits because of the physical dispersion of conducting molecules throughout a solid mass of nonconducting polymer chains.

The Innovative Technical Approach

The breakthrough that overcomes these three dimensional challenges is the invention of a “print and plate” process which includes a special “precursor” ink that is used to print the areas where the conducting metal is to be deposited. This controls the horizontal dimensions of width and length. The vertical dimension of metal thickness is controlled by using a proven high volume additive ‘plating’ process that deposits conducting metal only in the areas defined by the precursor ink. This precursor ink also creates stronger bonds between the conductor and the substrate which improves lifetime and eliminates adhesives and other bonding methods.

This combination of the innovative precursor ink and proven chemical and electrolytic plating processes results in a roll-to-roll manufacturing process by which flex circuit materials and flex circuit board layers with custom metal thicknesses can be produced at volume production prices. This mass customization approach can translate into supply chain cost savings of 50% to 75%, circuits that are 50% to 85% thinner, and circuit density increases that are at the state of the art.

There is a variety of innovations that have been developed as part of the commercialization of this print and plate technology. These innovations include: (1) design of a catalytic ink which serves as a delivery mechanism for a special catalytic compound. This delivery mechanism is advantageous because in addition to eliminating the need for adhesive materials and layers and expensive toxic tie coats, it also the pattern of where the metal is to be deposited. The ink solution can then be deposited as either a coating or in a pattern using a printing technique; (2) “tuning” of the precursor ink to a variety of coating/printing techniques to deposit the precursor ink; (3) a curing process which converts the catalytic compound molecules left behind from the dried ink into active catalysts for the metal for which the compound has been matched and selected. When the catalytic molecules have been activated, each molecule becomes a bonding agent between the substrate and the metal molecules in an electroless plating bath; (4) Variety of substrates for which the precursor ink was designed. The substrates included a wide range of films made of filled and unfilled polyimides, polyesters, polycarbonates, and rigid three dimensional parts such as glass plates, molded parts, and drawn fibers. This variety of substrate types and shapes creates the opportunity for metalizing for both electrical applications as well as decorative applications; (5) Variety in the types of metals that can be deposited by this technique; and (6) Metallization of the inside walls of vias that have been drilled into the flexible substrates at very early process stages.

Metalizing Via Surfaces

Metalizing via surfaces at the very earliest stages of a production process is an innovation that offers the elimination of several process steps that are currently embedded in the conventional manufacturing of flexible circuit boards that use subtractive and semi-additive processes. Typically vias are plated and filled at later stages in the flex circuit board layer manufacturing process because of the manufacturing processes associated with flex circuit materials that are either adhesive-based or vacuum sputtering on metal tie coats. Using the precursor ink technology described above, copper can be deposited on the inner surfaces of vias at the very earliest stages of a flex circuit production process.

The demonstration of using the print and plate method for vias is shown in Figures 1 through 3. In Figure 1, a microscopic picture of a via that is 35 micron in diameter and which is laser drilled in commercially available film of polyimide that is 25 microns thick is shown.

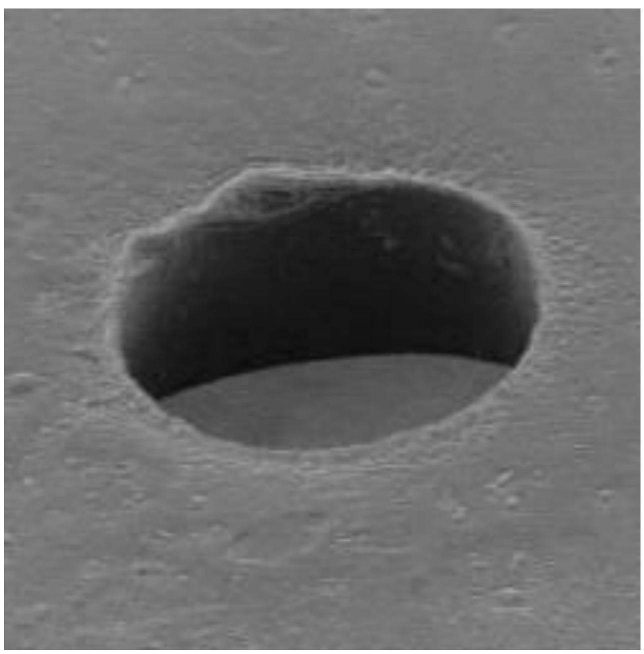

Figure 1: 35 micron diameter via in 25 micron thick polyimide

In Figures 2, a via of the same size is shown with a layer of copper that is approximately 1 micron thick that has been deposited using the Print and Plate process described above.

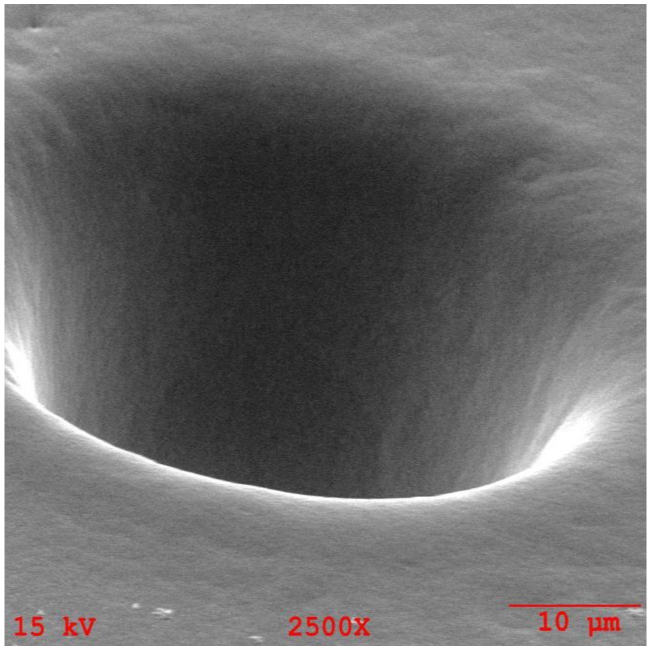

Figure 2: 35 micron via metalized with the Print and Plate Process

In Figure 3, a cross section of the via in Figure 2 is shown to highlight the degree of uniformity of the copper thickness from the surface of the polyimide to the inner walls of the via.

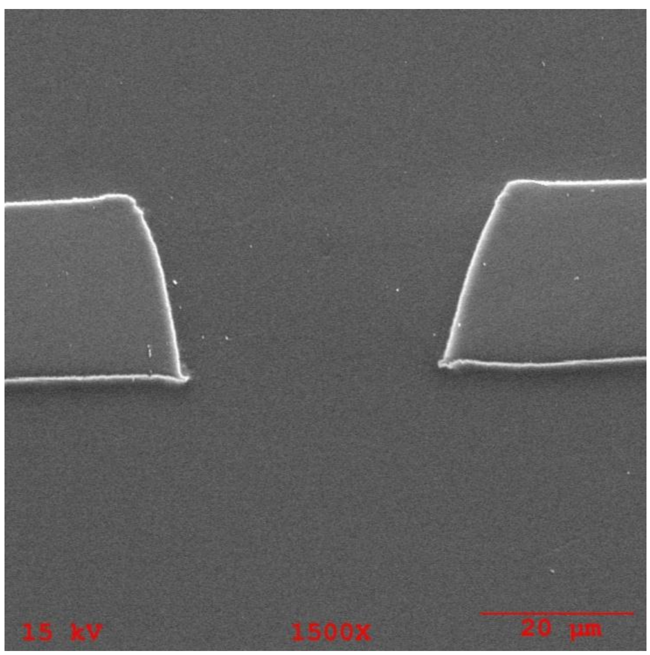

Figure 3: Cross Section of the Material in Figure 2 (35 micron diameter vias)

Potential Benefits

The significance of being able to deposit copper on the inner surfaces of vias in early stages of the production process is illustrated in Figures 4 and 5. Several later stage steps can be avoided when vias can be seed-coated with copper early in the process. The precursor ink process described herein allows this to happen whereas sputtered tie coat technology cannot.

In the illustration in Figure 4, the advantages of the print-and-plate method for pre-drilled vias over the conventional subtractive is clear: an entire iteration of imaging and etching is eliminated. The savings in cost and time and improvement in yield can be substantial. A cost model of the subtractive etch process indicates that savings in the direct costs of goods sold is in the range of 10% to 15% and up to 25% in reduction of cycle time.

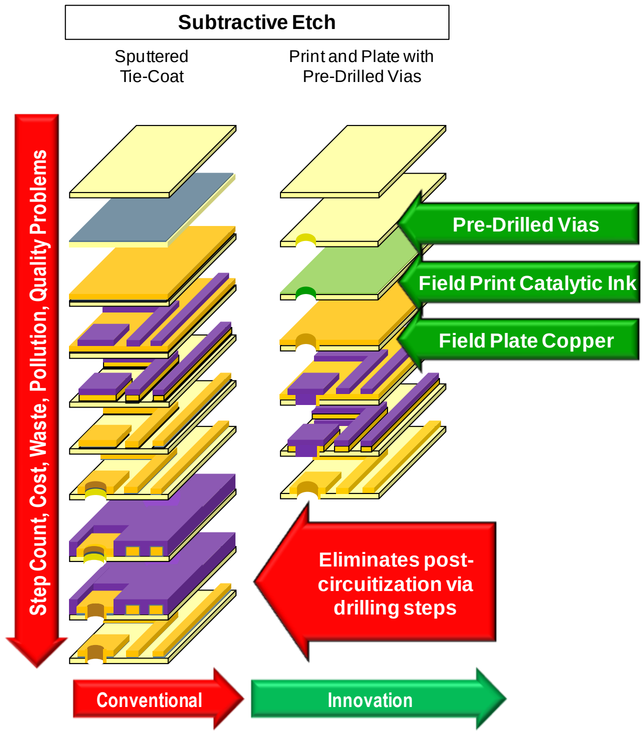

Figure 4: Comparison of Print-and-Plate of Pre-Drilled Vias for Subtractive Etch Processes

The benefits of the print-and-plate method for pre-drilled vias within the semi-additive and additive methods are also compelling. In fact, without the ability of depositing copper on pre-drilled vias, the semi-additive and additive methods are impractical in most cases. These benefits in eliminating process steps that translate into cost and time savings are illustrated in Figure 5.

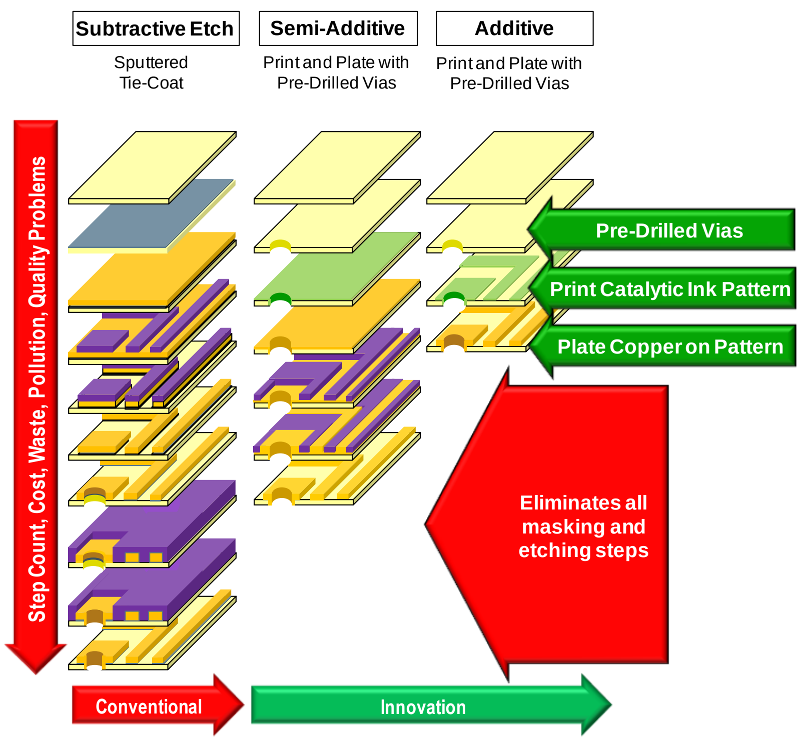

Figure 5: Comparison of Print-and-Plate of Pre-Drilled Vias for Subtractive, Semi-Additive and Additive Processes

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Including the value of this early via plating capability of this new process increases the favorable comparison with other flex circuit production technologies. An updated summary of these comparisons is shown in Table 1.

Table 1: Comparison with Other Technologies

	Vacuum Sputtered	Cast-on	Polyimide Laminated	Conductive Ink	Precursor Ink Print and Plate
Process	Subtractive or Semi-Additive	Subtractive	Subtractive	Additive	Subtractive or Semi-Additive
Adhesive	None	None	Yes	Yes (included in ink)	None
Electrical Conductance	High	High	High	Low	High
Tie-coat	Chrome, nickel, other	None	None	None	None
Metal Thickness	Custom build up	Fixed by foil thickness	Fixed by foil thickness	Fixed by Ink Thickness	Custom build up
Peel Strength	High	High	High	Low	High
Via metallization	Post process	Post process	Post process	Post process	In-process
Environment Impact	High	High	High	Low	Low
Cost	High	Moderate	Moderate	Low	Moderate

Summary

The key advantages of the innovative copper deposition process for flexible circuit materials described above include (1) that it eliminates the need for multiple plating steps to plate vias after they have been formed into circuitized materials, (2) that it can deposit copper on the surfaces of bare base material and in the interior of vias that are pre-formed in the base material, (3) that it eliminates several expensive process steps normally associated with conventional copper coating techniques, and (4) that it produces superior adhesion without the need for a tie coat of chromium or nickel. The process steps have been implemented with a roll-to-roll manufacturing process as well as in a discrete panel process. Excellent adhesion to the base material has been achieved along with good surface insulation resistance (SIR) and other pertinent properties.

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Presentation Outline

- Introduction
- Need
- Approach
- Benefits
- Comparison

Introduction

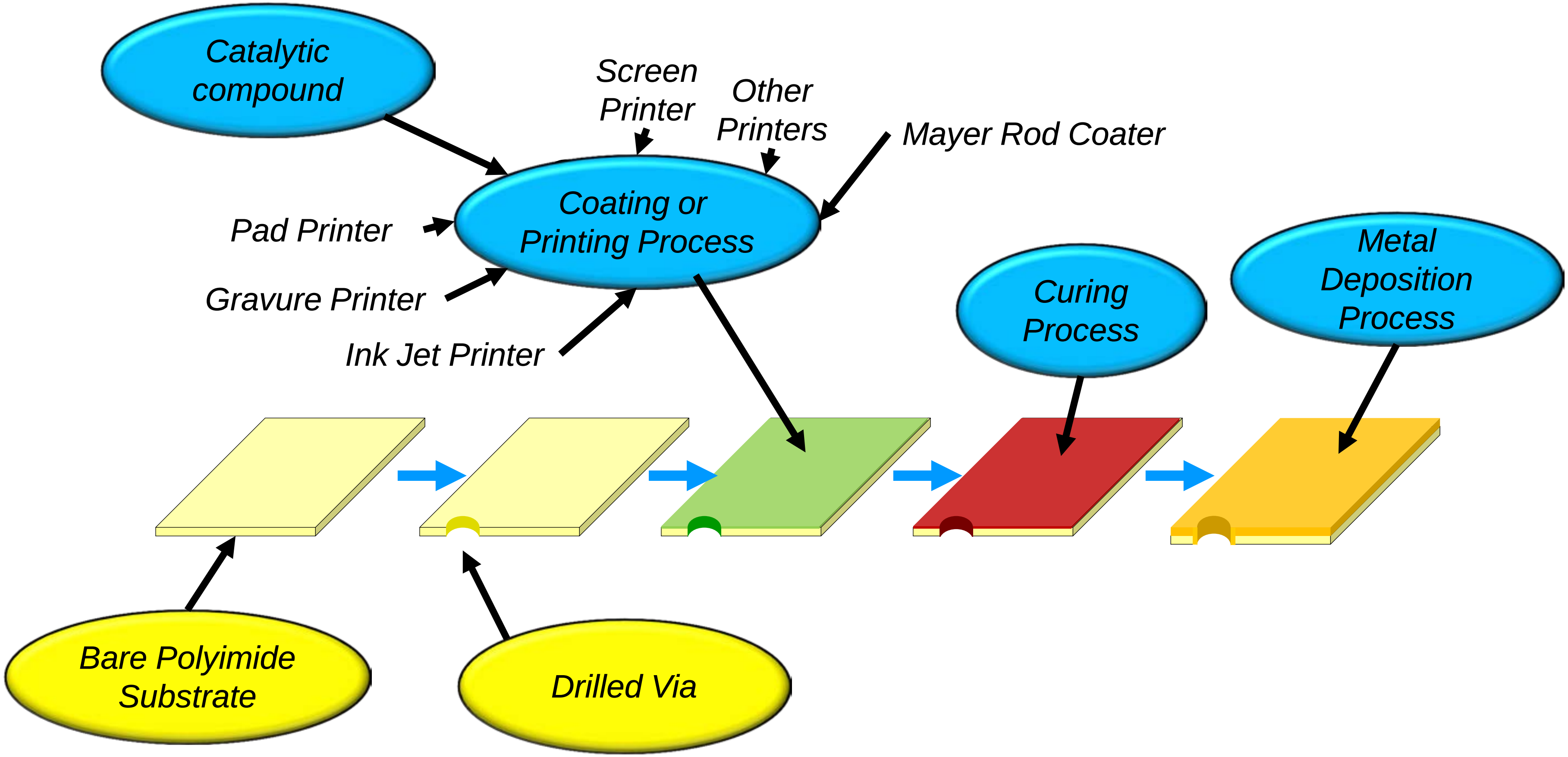
Our History

- SRI: Innovation in printing metals
  - Over a decade of client projects and IP generation
  - Innovation in printing metals (Au, Cu, Ni, Pd) on substrates (PI, PE, Paper, Fiber, …)
  - Applications (Interconnects, Microelectronics, RFID tags, Flexible, conformal surfaces, Decoration)
- CSL: innovation, quality, eco-friendly
  - CSL Formed in 1986 expert in high quality metal chemical and electrochemical deposition technology
    - Web and Spin coating, Sputter deposition, Electrophoretic coating, Electroplating, Electroless plating

Print-and-Plate Innovations

1. Design of the precursor ink.
2. “Tuned” ink to variety of printing methods
3. Ink curing process.
4. Substrate variety.
5. Metalization variety (Cu, Au, Ru, Pd)
6. Metallization of the interior of vias

Innovations…With Via's



The Need

Needed by Flex Circuit Industry

- Thinner metal layers (18 μ ➔ 2 μ)
- Greater density (<25 μ lines and spaces)
- Less waste and more eco friendly
  - Eliminate chromium from sputtered tie-coat
  - Eliminate wasted copper and etching solution
- Higher quality
  - No adhesive
  - More bends, higher temperature, stronger bonds
- Lower cost

The Approach

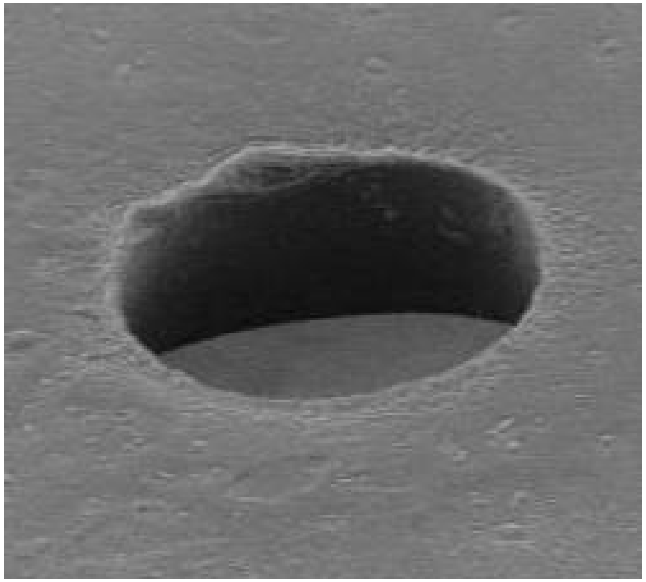
Our Approach

- Technology Approach: Print and plate flex circuit materials in three dimensions
  - –Print special precursor ink to control x and y (line density)
  - –Plate metal to control z (thickness)
- Product Approach:
  - –Current: High quality flex circuit materials
    - Thin, custom, roll-to-roll, no tie coat, field coated flex materials
    - Build thickness to order; differential plating
  - –Next: Custom patterned flex circuit layers

Precursor Ink Capabilities

- Key Invention: Precursor ink
  - A liquid with a catalyst in solution
  - Can be applied in cost effective roll-to-roll process
  - Catalyst pattern (nm thick) defines copper pattern

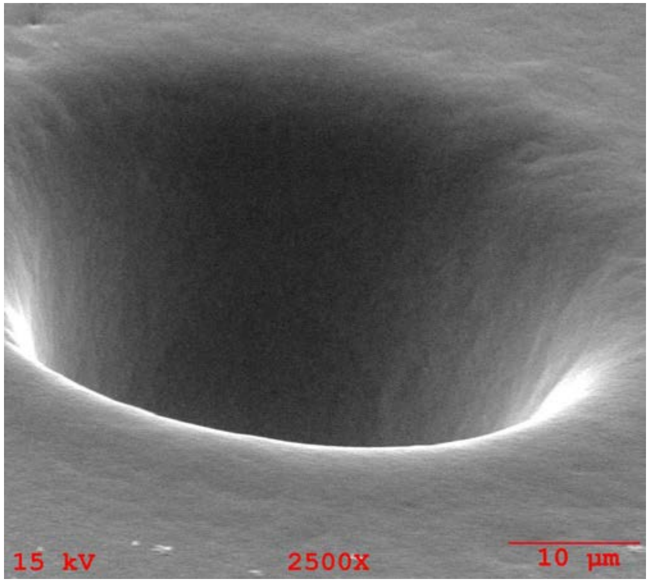
Via in Polyimide



35 micron diameter via

Bare polyimide

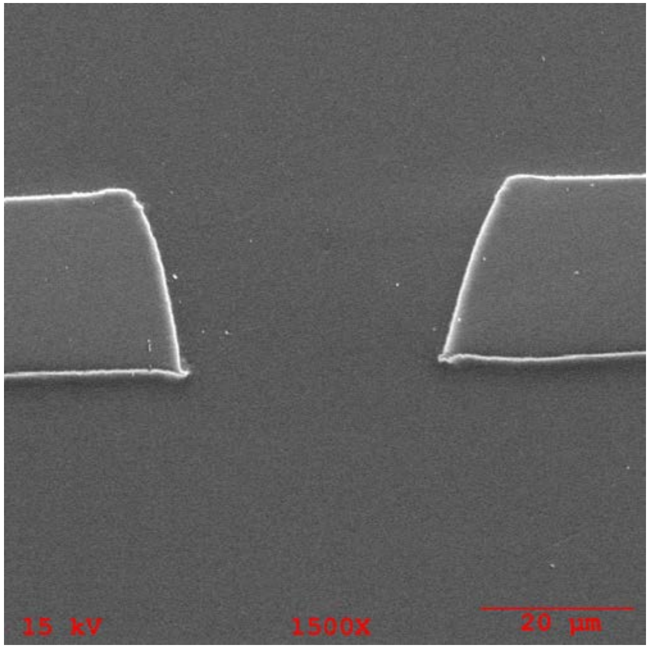
Cu in Via



35 micron diameter via

Copper is 0.2 micron thick

Cross Section of Via with Cu



35 micron diameter via

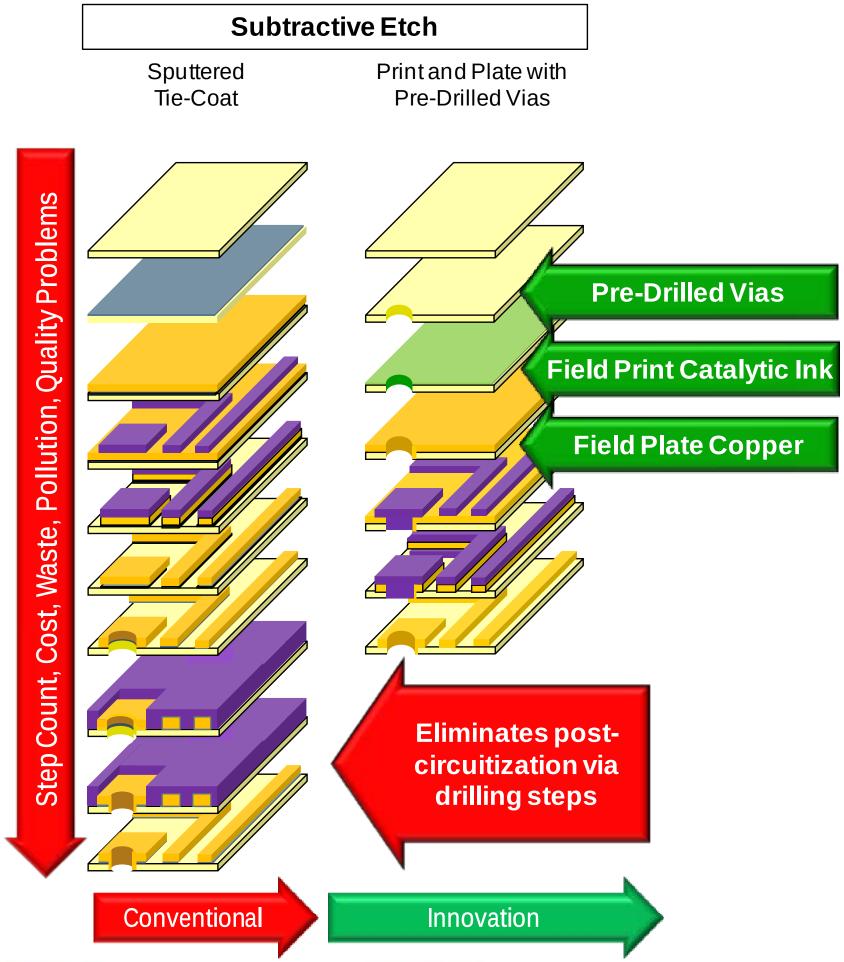
Copper is 0.2 micron thick

The Benefits

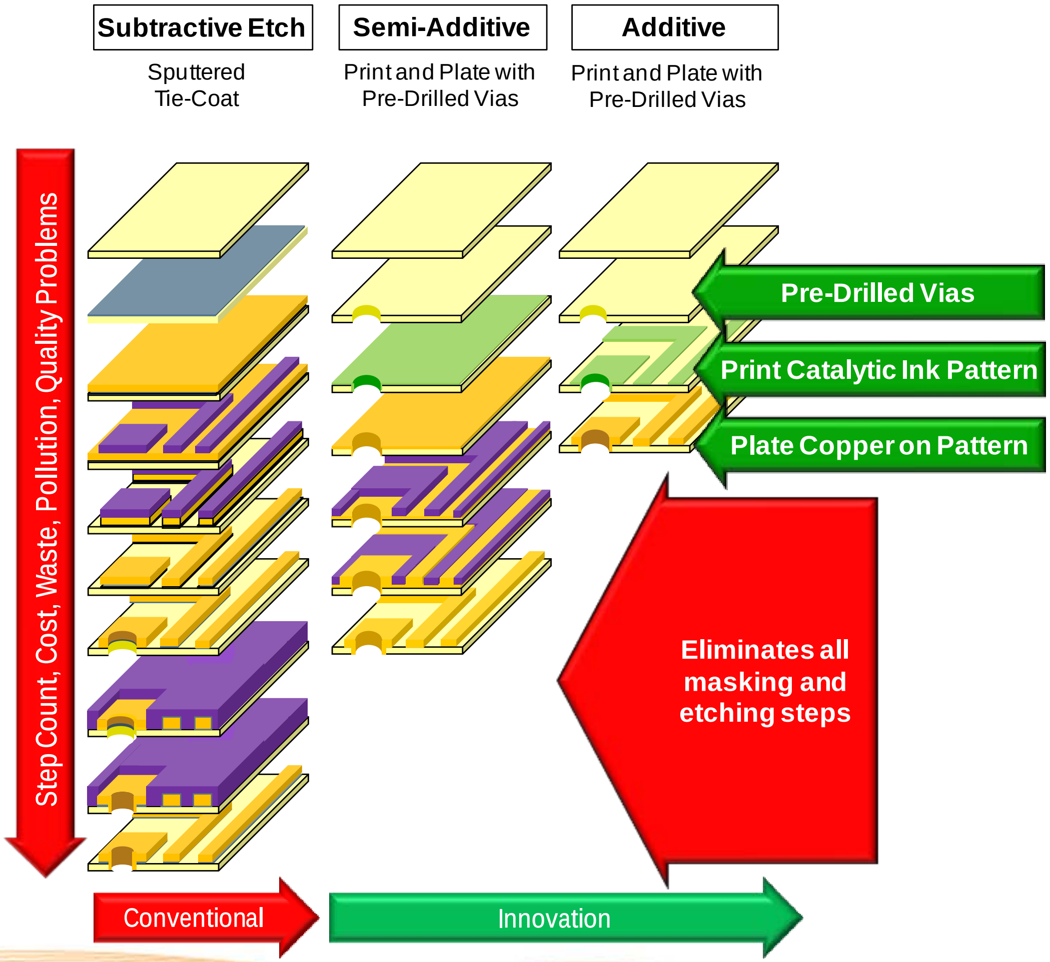
The Benefits

- Benefits
  - Green, clean tech process for flex circuits
  - Custom materials at volume prices
  - Reduce process costs of flex circuits by 50% to 75%
  - Decrease thickness by 50% to 85%
  - Cutting edge circuit density

Takes Cost Out of Subtractive Etch Processing



Makes Additive Process Practical and Takes Significant Cost Out



Competitive Technology Comparison

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Summary and Conclusions