

Factors Affecting the Adhesion of Thin Film Copper on Polyimide

David Ciufu, Hsin-Yi Tsai and Michael J. Carmody
Intrinsiq Materials
Rochester, NY

Abstract

The use of copper foils laminated to polyimide (PI) as flexible printed circuit board precursor is a standard practice in the PCB industry. We have previously described[1] an approach to very thin copper laminates of coating uniform layers of nano copper inks and converting them into conductive foils via photonic sintering with a multibulb conveyor system, which is consistent with roll-to-roll manufacturing. The copper thickness of these foils can be augmented by electroplating. Very thin copper layers enable etching fine lines in the flexible circuit. These films must adhere tenaciously to the polyimide substrate. In this paper, we investigate the factors which improve and inhibit adhesion. It was found that the ink composition, photonic sintering conditions, substrate pretreatment, and the inclusion of layers (metal and organic) intermediate between the copper and the polyimide are important.

Ink factors include the intensity of photonic sintering. Better sintering leads to better cohesive strength of the nano copper layer. The ink solvent and the dispersant used to suspend the nano particles are significant both for adhesion and the colloidal stability of the dispersion. Pretreatment of the substrate by plasma roughening did not improve adhesion. We describe the effects of chromium and nickel interlayers which are typically used in standard foil laminates. Finally, we describe the types of peel testing used to assess adhesion.

Introduction

The goal of our ultra-thin film project is to create a thin (1-2 micron) film of uniform copper on flexible polyimide for application to flex circuits. Ultra-thin films allow very narrow copper lines on patterns created by photolithography, plating, and etching. Figure 1 depicts the invented process.



Figure 1. A process for preparing very thin copper foil on polyimide.

A very thin layer of nano copper ink is created on polyimide by coating techniques. A picture of a coating made in a roll-to-roll (R2R) manner on a slot die coating machine is shown at left in Figure 2. After drying the ink (done by air impingement here), a film of copper nano particles in dispersant/binder of about 0.5-1.0 microns thick is produced. This film can be turned into a continuous film of conductive copper metal by photonic sintering with a flash lamp system. There have been developed special R2R machines with moving conveyors, multiple flash bulbs, and algorithms to control and interleave flashes to give uniform sintering of the coating[2]. On the other hand, the lab scale coatings are made by using an automatic Mayer bar coater (Fig.2, right), dried in a vacuum oven, and sintered by a single flash lamp unit in the lab. The resulting copper films are less uniform than the ones generated by the R2R process, and banding where the flashes overlap is usually observed. Alternatively, a uniform conductive copper film can be generated by sintering by immersing in a formic acid / argon reducing atmosphere at 190°C for an hour (Fig.3).

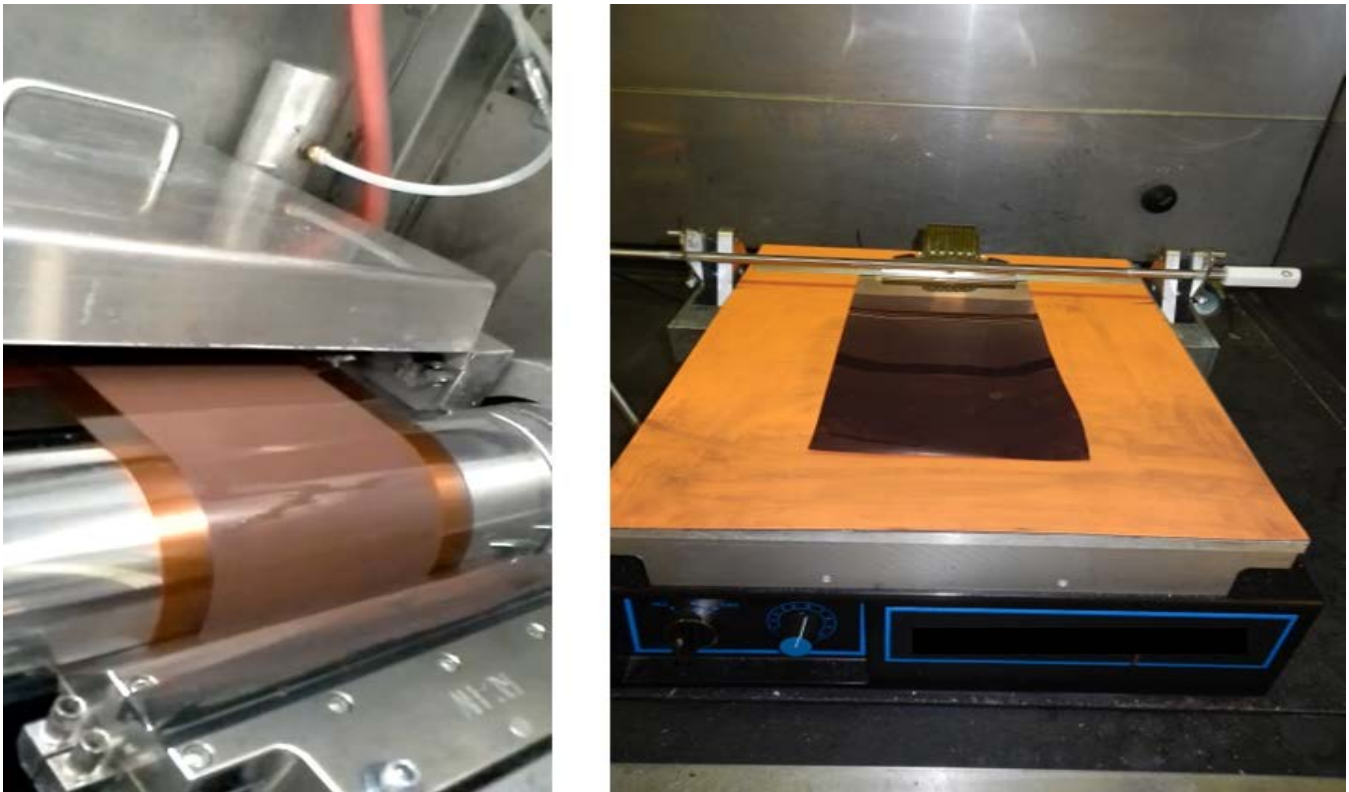


Figure 2. Ways to coat uniform layers of nano copper ink.

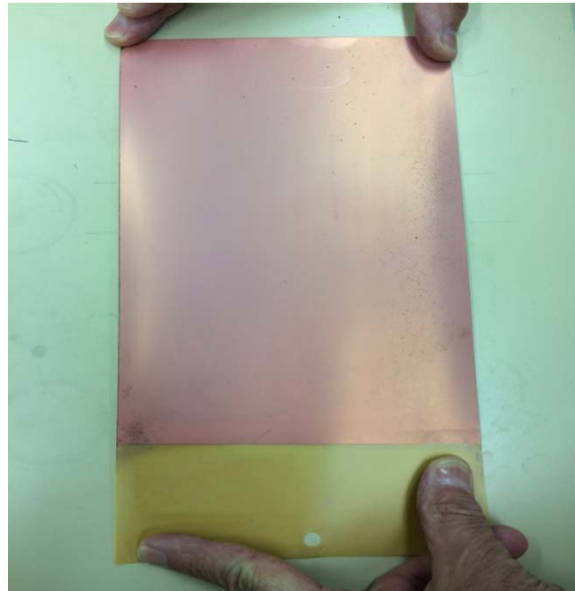


Figure 3. A uniformly sintered Meyer bar coating of nano copper ink on an epoxy BT rigid substrate.

This conductive layer can be treated in an electroplating bath to give copper anywhere from 3-50 microns of copper. As stated earlier, 1-2 microns thick would be best for masking off the sintered layer, electroplating a pattern, removing the mask, and etching off the unwanted copper. Since etching is isotropic, the sides of the plated traces will etch as well at the tops, and thinner traces give less under-cutting and straighter side walls. Using the ultra-thin film process, straight side walls of features on the etched film can be achieved, as shown in Figure 4. Present methods of creating these 1-2 micron films involve sputtering or etching thick foil laminated layers and are very expensive.

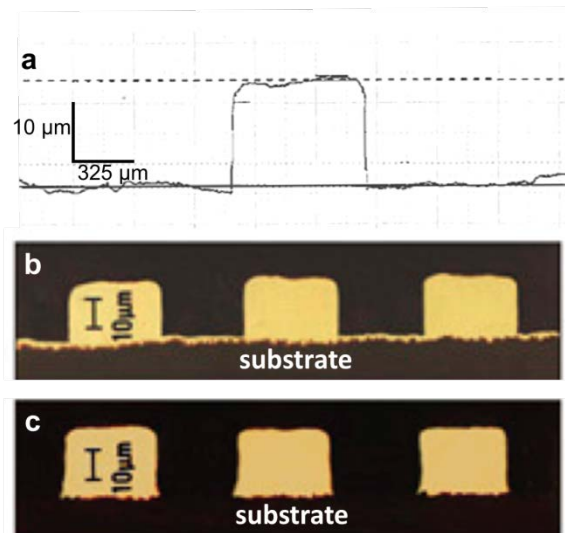


Figure 4. A profilometry graph of an etched trace (a), and cross section photographs of plated (b) and etched (c) traces.

In the present paper, we discuss the adhesion of the thin copper films on flexible polyimide substrates created by ultra-thin film process, and the possible factors to improve the adhesion.

Methodology

The adhesion of ultra-thin films was tested by the ASTM3359 cross hatched tape test in which a pattern of horizontal and vertical cuts spaced 1 mm apart are made in the copper layer by a blade (a razor blade was used). A special tape is adhered to the cross-hatched area and peeled off at about 180°.

To test the adhesion of the patterned, plated, and etched copper layers, a peel test following IPC-TM-650-2.4.8 is routinely used in the printed circuit industry. Here special coupons >30 microns tall are created. They are 1 mm wide X up to 96 mm long, with a wider tab at the end for attaching by a clamp to a force gauge. The trace is peeled in a controlled manner at 90° to the surface of the PI and the force measured as a function of peel length. A photo of such a sample is shown in Figure 5.

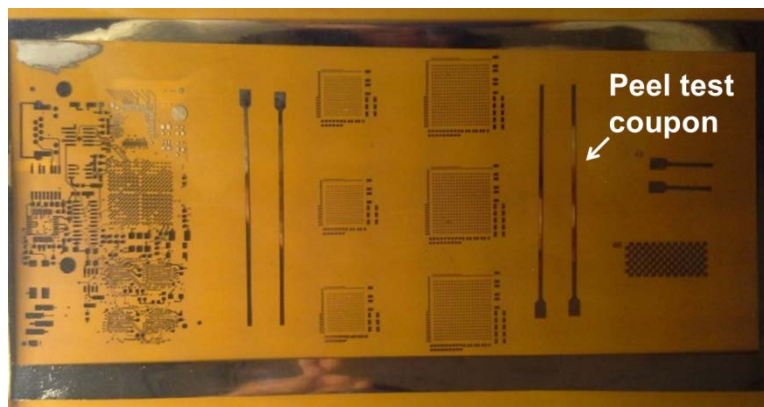


Figure 5. A plated, etched sample of nano copper ink on polyimide showing the peel strength coupon.

Data and Results

One of the attractive features of this ultra-thin film process has been that the coated, dried, and sintered 0.5 micron copper layer adhere very well to polyimide. Due to the fine thickness of the films, the ASTM3359 cross hatched tape test has been applied to test the adhesion of the coatings. In the present study, the tested thin film samples were prepared by a lab scale preparation, i.e., Mayer bar coating, vacuum dry and single flash lamp sintering, and it was found that none of the sintered copper is removed by the tape.

However, for the patterned, plated, and etched copper layers, it was found that these 1 mm wide traces have highly variable adhesion. A peel force of about 10 N/cm is acceptable in the industry, and there have been samples that ranged from 0 N/cm (came off in the etching bath) to 8 N/m. So, a sintered copper layer was used that adheres very well to polyimide, but when that layer is masked, plated, and etched, the resulting (>30 micron) layer *sometimes* does not adhere very well. It is instructive to point out that the plated etched area is >30 microns thick because the peel coupons must be that thick to avoid tearing when connected to the peel test apparatus and pulled.

In order to understand the possible sources for this variable adhesion that are seen for plated and etched samples, we have investigated a number of factors which might affect the adhesion in our system. First, we investigated the flash sintering conditions. Well-sintered layers usually conduct the best and have the best adhesion. Additionally, we have mentioned already that sintering large areas of coated ink by overlapping repetitive flashes from a single bulb shows a darker band in the overlap area, and it has been found that the overlap area does not exhibit as good adhesion as the more copper colored area from a single flash (data not shown). The SEM images from the copper colored area and darker band (Fig. 6) clearly showed the difference in particle morphology, i.e., less particle necking and densification in the dark area. The result indicates that the sintering condition of the nano copper ink is important to the adhesion. This also points out the criticality of using a flash apparatus specifically designed to minimize such banding.

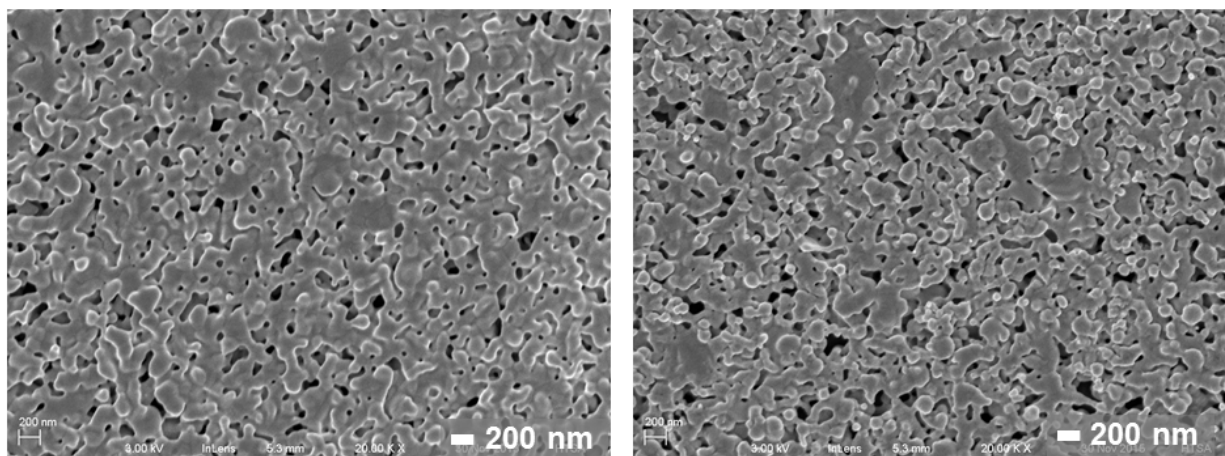


Figure 6. SEM images of the copper nano particles on copper colored area (left) and darker band (right) of a coated ink sample sintered by repetitive flashes.

When the coated and dried ink is treated with the flash lamp system, the binder/dispersant decomposes and flashes off allowing the copper nano particles to sinter via necking. Vapors from this process can be observed on sintering. However, electron micrographic evidence suggests that some binder is left at the copper/substrate interface of a nano copper film plated up to $\sim 5 \mu\text{m}$ thick. As the plated film was peeled off, the deformed polymer fibers (by the peel force) were left on both nano copper (Fig. 7a, 7b) and the substrate (Fig.7c). Furthermore, the polymer layer left on the substrate (visible by the naked eye) can be wiped off by good solvents but not by bad solvents of the binder. The results clearly indicate the presence of binder/dispersant at the end of the sintering and plating process (data not shown).

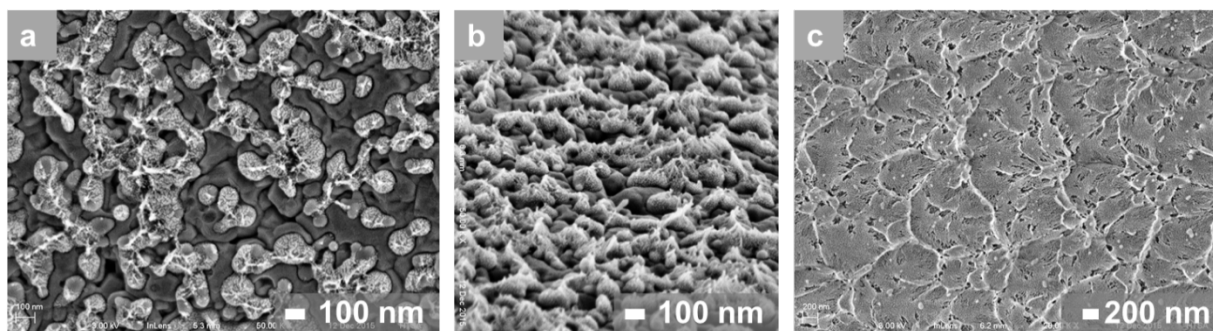


Figure 7. SEM images of gold sputtered samples of a sintered and plated copper film, peeled from the substrate. (a) Top view of the peeled film. (b) Tilted view of the peeled film. (c) Top view of the substrate underneath.

The results suggest that the dispersant/binder is playing an important role as an adhesive layer at the interface, therefore affecting the adhesion. To investigate the binder effect, we examined a number of binders of different chemical structures and different solvent systems for their ability to disperse the nano copper and to provide subsequent adhesion. A list of tested dispersant/solvent combinations is shown in Table 1. Five of these provide sufficient dispersion stability to allow further coating and adhesion testing. These inks were Meyer bar coated, vacuum dried, and flash sintered into 6X9 inch samples in the lab and the resulting uniform copper samples were sent to a local printed circuit house for preparation of peel strength coupons by masking, plating, and etching. An assessment of the adhesion of these materials is shown in Table 2.

Table 1. A list of tested dispersants and solvents.

Dispersant	Solvent	Stable ink
Polyvinylpyrrolidone	DEGBE	Yes
Polyoxyethylene octyl phenyl ether	EG/1M2P	No
Polyvinylpyrrolidone-polyvinylacetate copolymer	EG/1M2P	No
Polyvinylpyrrolidone-polyvinylacetate copolymer	DEGBE	No
Polypropylene carbonate	propylene carbonate	No
Polypropylene carbonate	N-methyl-2-pyrrolidone	No
Polypropylene carbonate	DEGMEEA	No
Hyperdispersant A	DEGMEEA	No
Hyperdispersant A	DEGBE	Yes
Polyvinyl butyral	DEGBE/MMB	Yes
Dispersant B	DEGBE	No
Polyether polyamide	DEGBE	No
Polyalkyleneoxy terminated polyamide	DEGBE	No
Polymethacrylate copolymer	DEGBE	Yes
Polymethacrylate copolymer	DEGBE/butanone	Yes

Table 2. Maximum peel strength of 1 mm wide peel test coupons on the plated and etched copper nano ink coatings (N=2-3).

Dispersant	Solvent	Max. peel strength (N/cm)		
		1	2	3
Polyvinylpyrrolidone	DEGBE	4.4	4.4	---
Hyperdispersant A	DEGBE	6.8	0	4.5
Polyvinyl butyral	DEGBE/MMB	0	0	---
Polymethacrylate copolymer	DEGBE	8.0	3.8	3.4
Polymethacrylate copolymer	DEGBE/butanone	0	0	---

The maximum peel strengths of 2-3 peel test coupons on the plated (to ~30 μm) and etched films are recorded and listed in Table 2. Two samples showed very poor adhesion of the final film; zero peel strength is assigned as the traces fell off. For the other three samples, the numbers are quite variable, indicating non-uniform adhesion on the 6X9 inch coatings. The non-uniformity can be attributed to the sintering by overlapping repetitive flashes from a single bulb, resulting in less particle necking in the overlap area, as mentioned previously.

Another possible reason is the contamination on the PI surface (dust, grease...etc.), which largely affects the surface energy and therefore the thin film formation during ink drying. Interestingly, the last two inks on the table that both employed polymethacrylate copolymer as dispersant/binder, showed very different adhesion results as different solvents were used. This suggests that the configuration of the polymeric dispersant/binder in the ink is possibly important to the adhesion. Overall, it is believed that we can further improve the adhesion by testing more binders that have similar chemical structures and properties with polyvinylpyrrolidone, hyperdispersant A and polymethacrylate copolymer.

It has been reported in the literature that the adhesion between copper and polyimide can be improved by applying a thin layer of chromium[3,4] It has been attempted to sputter a thin (<100 nm) layer of metal like Cr, Ti, or Cr/Cu as a tie layer on plasma treated polyimide substrates (20% O_2/Ar , 3 min at 15 mtorr), upon which to coat the ink. We found that there was a great deal of difficulty sintering these samples with a metal layer underneath, while no significant difference was observed on the plasma treated (control) sample, as shown in Figure 8. The coated copper developed holes on sintering show the sputtered metal underneath. The unexpected loss of adhesion might come from the nature of the deposited copper on the metal interlayer. In the literature, the metal layer promotes the adhesion of electron-beam evaporated[4] or sputtered[3] pure copper, but the copper nano ink includes dispersants/binders that may interfere with the interface. Since these sputtered samples had very poor adhesion at this point, none were masked, plated, and etched.

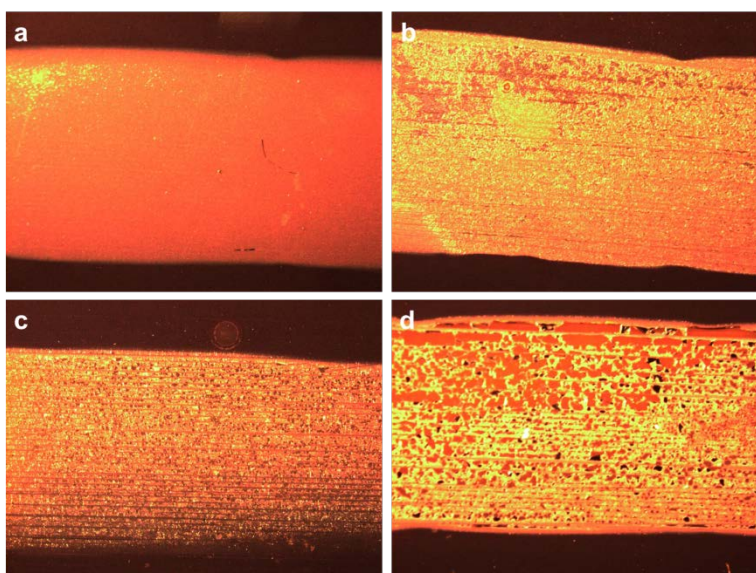


Figure 8. Micrographs of coated nano copper films on (a) plasma treated PI; (b) PI with 5-7.5 nm of chromium coating; (c) PI with 7.5 nm of titanium coating and (d) PI with 7.5 nm of chromium/100 nm of copper coating.

Surface cleaning and modification by physical and chemical means are often used to promote adhesion. A commercially available polyimide substrate, which was invented to promote the adhesion to copper, has been tested. However, we could not find significant improvement in adhesion comparing to regular PI substrate (Table 3). It is argued that the stronger adhesion to copper can be achieved through chemical functionalization and physical roughening of polyimide surfaces, by plasma or alkaline treatment[5-7]. However, the nano copper film on the plasma treated PI (Fig. 8a) did not show stronger adhesion after plating and etching, compared to the film on untreated PI (data not shown). Further investigation on the effect of potassium hydroxide (KOH) treatment is in progress.

Table 3. Maximum peel strength of 1 mm wide peel test coupons on the plated and etched copper nano ink coatings on different PI substrates (N=2-3).

Polyimide	Max. peel strength (N/cm)		
	1	2	3
Regular	4.4	4.4	---
Modified	4.8	5.6	5.1

We have found so far that sintering condition and ink formulation (binder/solvent selection) have more impact on the adhesion of plated and etched films, while the surface modification of PI substrate does not seem to make much difference. We believe that in the system we use, the binder layer remaining at the interface after sintering is acting as an adhesive layer, and the adhesion failure happens between the nano copper layer and the binder layer. The surface modification of PI may promote the adhesion of the binder layer contacting with PI, but does not prevent the adhesion failure between nano copper layer and the binder layer. Sintering condition plays a complex role here, since it not only affects the connection between copper nano particles, but also the decomposition and therefore the remaining binder in the final film.

The fact that the sintered nano copper layer adheres well on PI but not after plating and etching makes us consider if the plating/etching chemistry is causing the adhesion failure. The sintered copper layer is not entirely homogeneous. As shown by the SEM image of a sintered trace (Fig. 9a), there are voids in the sintered copper film. The sintered copper film which densifies as copper nano particles are connected by necking. At the same time, the voids between the nano particles join to form larger voids. This explains why the conductivity of this sintered copper by this technique is about 10% that of pure copper wire. When plating those voids are filled in by much more uniform pure copper as shown in Figure9b. Since this image is from the substrate facing side of a trace peeled from the PI, the presence of plated copper clearly indicates that the plating solution can get into the voids and all the way down to the PI substrate. If there is a negative effect of plating solution on the interface, the solution certainly has access to it. Strategies to minimize the impact of the plating/etching chemistry, such as mixing binary nano particles to create denser packing, will be further investigated in the near future.

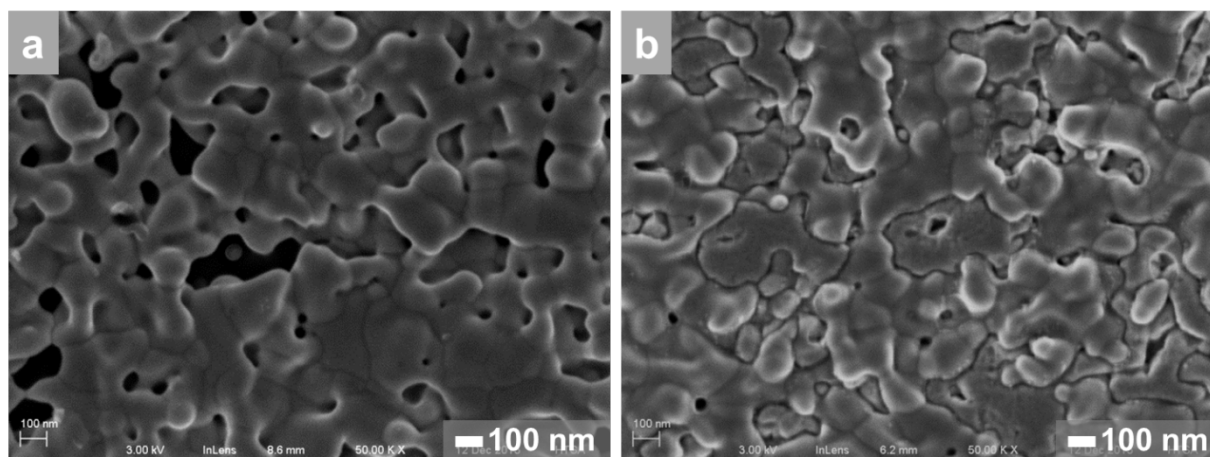


Figure 9. SEM images of (a) a sintered nano copper coating and (b) the substrate facing side of the same coating after plating to ~5 μm .

Conclusions

The ultra-thin film process is designed to put thinner copper cladding on both flexible and rigid printed circuit laminates than is currently available, by coating a 0.5~1 μm nano copper ink layer. There has been demonstrated excellent quality of etching on the patterns created by standard masking, plating and etching techniques. The adhesion is significantly affected by sintering condition and ink formulation, while not observed by the surface modification of PI substrate in the system. A few binders/dispersants have been found to give good ink stability and reasonable adhesion. It is concluded that the binder/dispersant layer between PI and nano copper is responsible for the adhesion, and the accessibility of the plating/etching chemistry toward the interface may determine the adhesion if it has any negative effect on the bonding at the interfaces. Overall, the technique provides the ability of the industry to greatly reduce minimum feature size and to also improve the performance of high speed electronics.

Acknowledgements

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Ultra Thin Copper on PCB Substrates

A Novel approach using Nano Copper Ink

David Ciufu, Hsin-Yi Tsai & Michael J. Carmody

Intrinsiq Materials

Ultra Thin Copper on PCB Substrates

- 1 Micron copper foils on Flexible and Rigid Substrates using Nano-Copper Inks.
- 3 Step Process to apply the Ultra Thin Coating



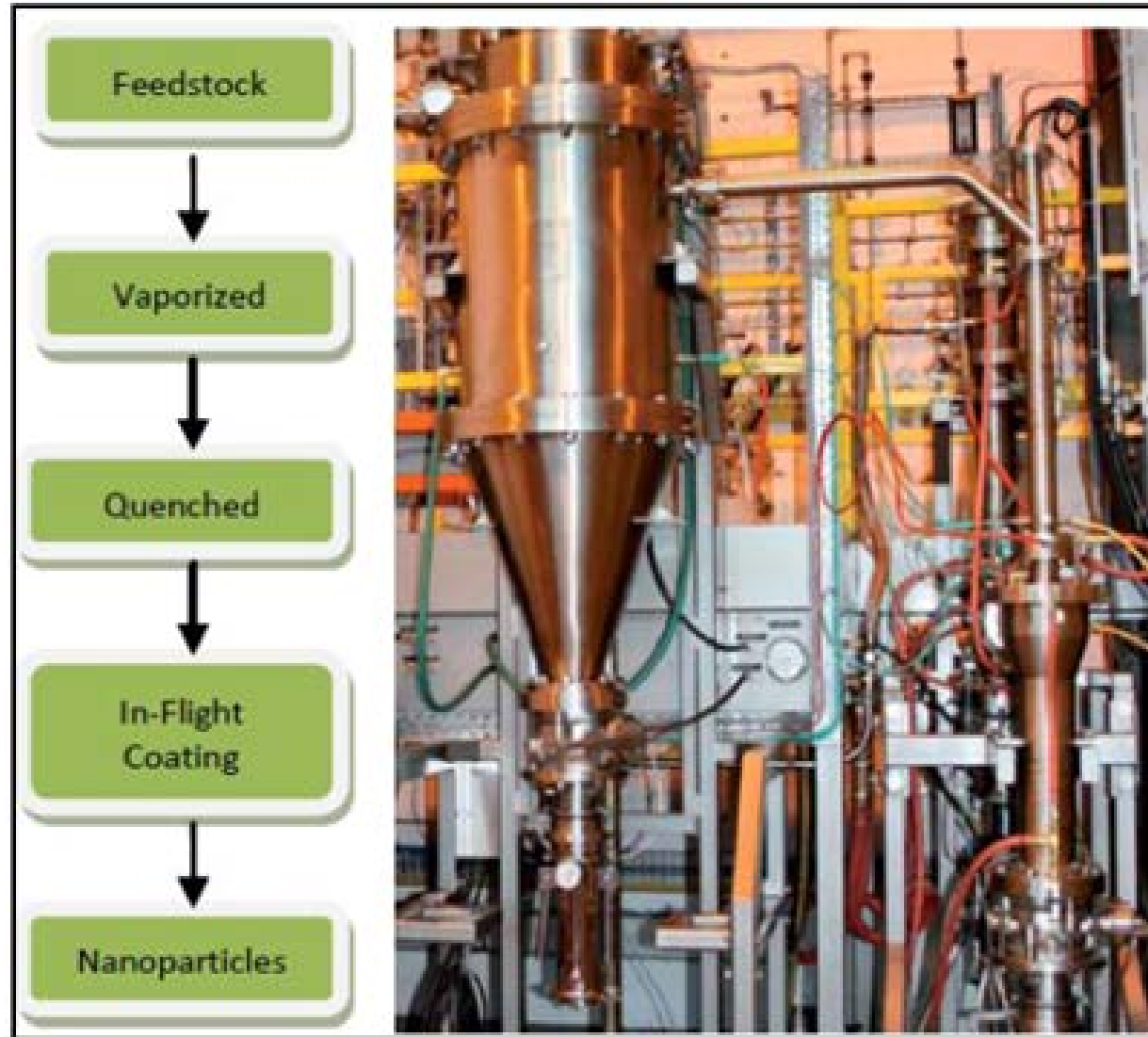
How important is thinner copper?

- More Precise Etching
 - Finer Lines
 - Narrower Spaces
 - Straighter side walls
- Less Waste
 - Current Techniques include etching down thicker foils or laminating using heavy copper carrier sheets.

How Does Nano Copper work as a thin film coating

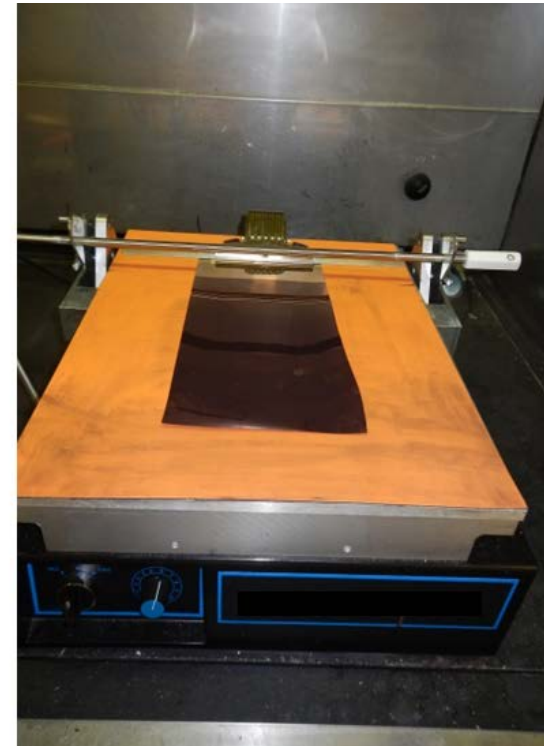
- First step is to create proper sized copper nano particles and coat them with a proprietary protective film
- This coating prevents agglomeration and oxidation.
- Allows for uniform dispersion in a binder / solvent

Plasma Generation of Nano Copper



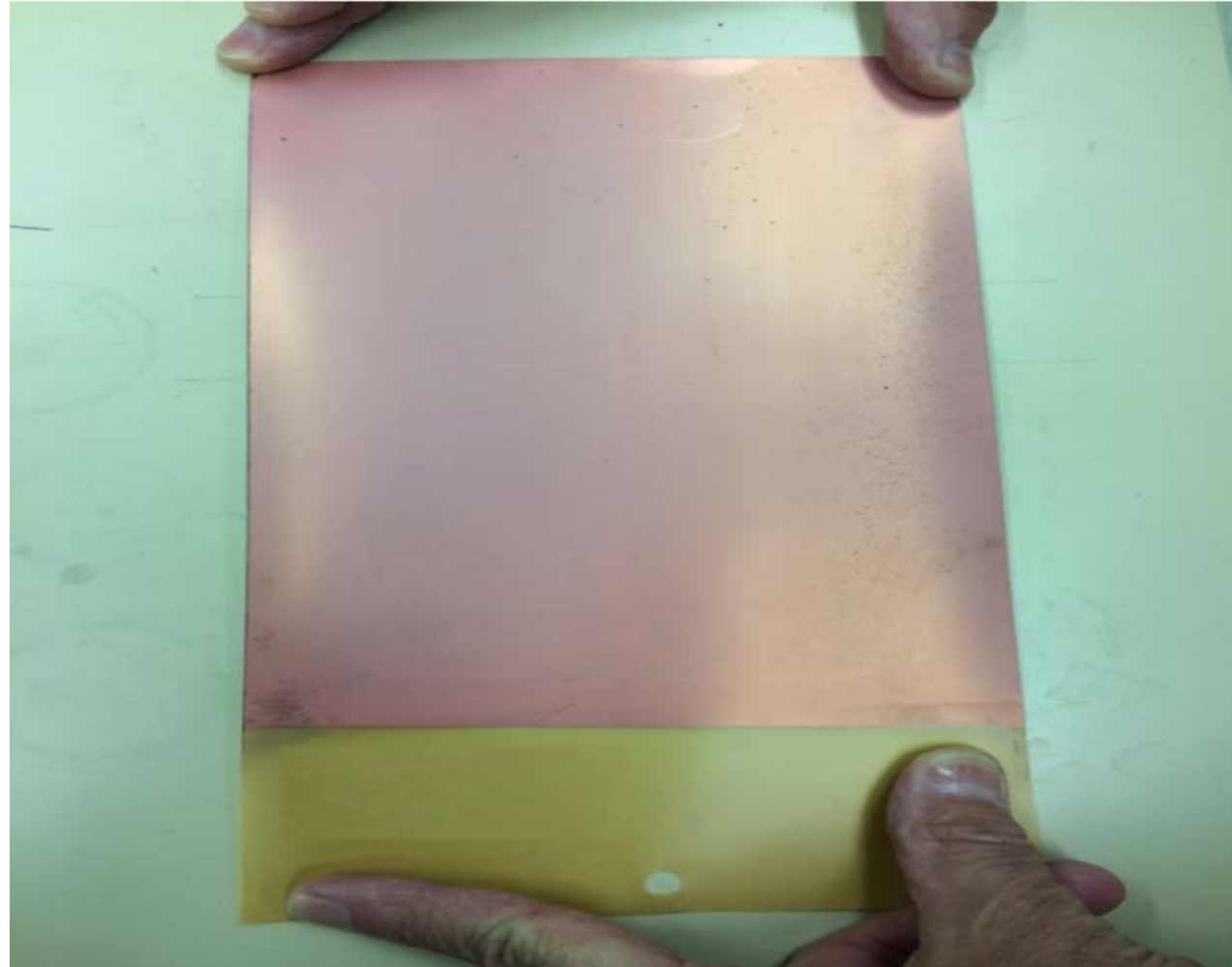
Methodology

- Coat substrate with Nano Copper Ink using process such as Slot Die Coating or Meyer Bar
- The coating is then dried and photonicallly sintered using a flash lamp



1 Micron Copper coating

- Uniformly Sintered Copper on Rigid BT Epoxy Substrate

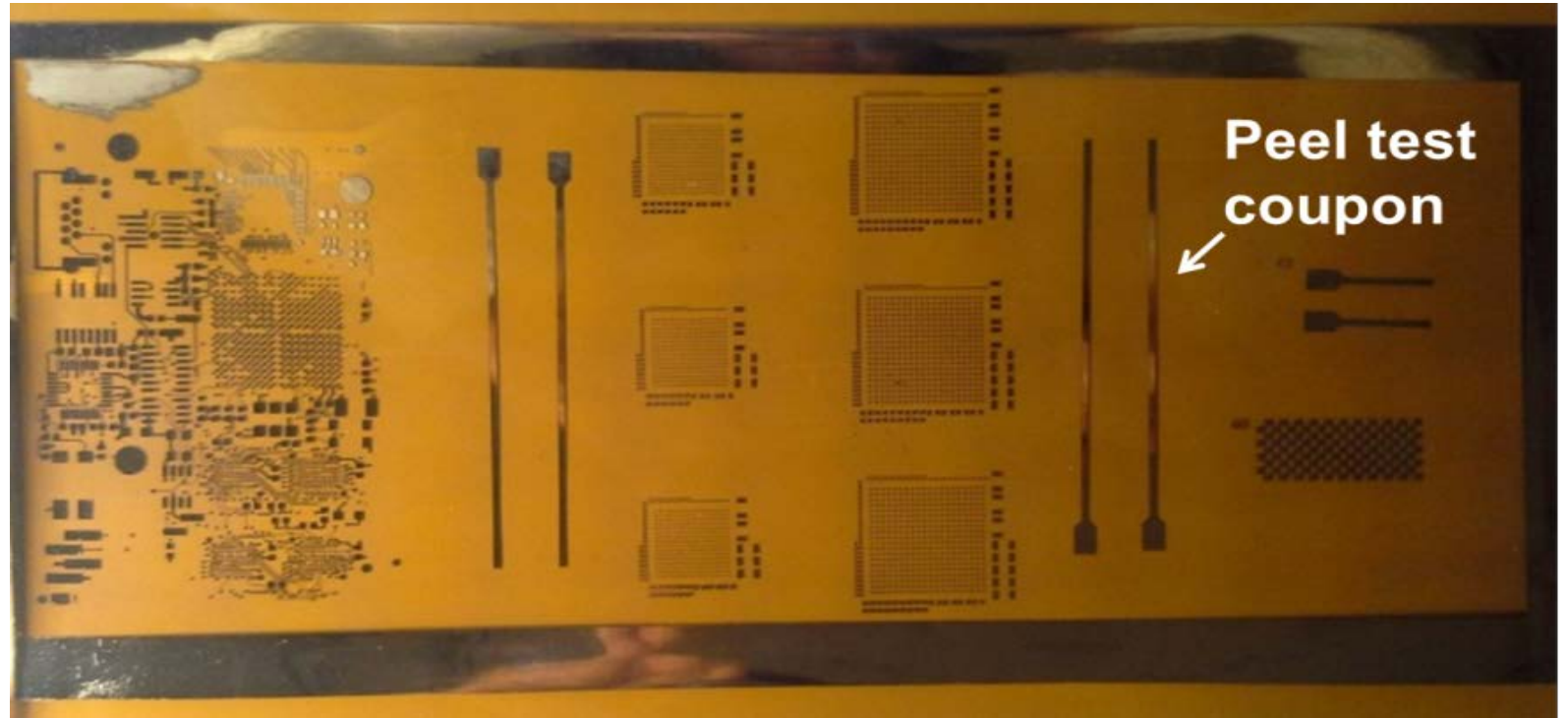


Testing the Coating

- The 1 Micron Copper needs to survive standard printed circuit processing.
- 6 X 9 inch samples of flexible and rigid substrates were created by using Meyer bar.
- Samples were dried then flash sintered
- The materials were sent to a local PCB shop for processing.

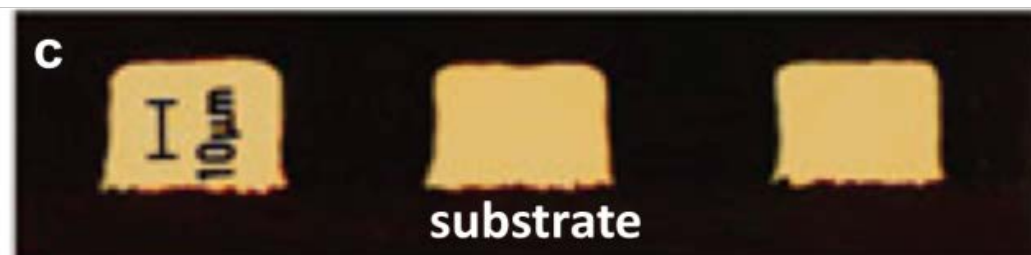
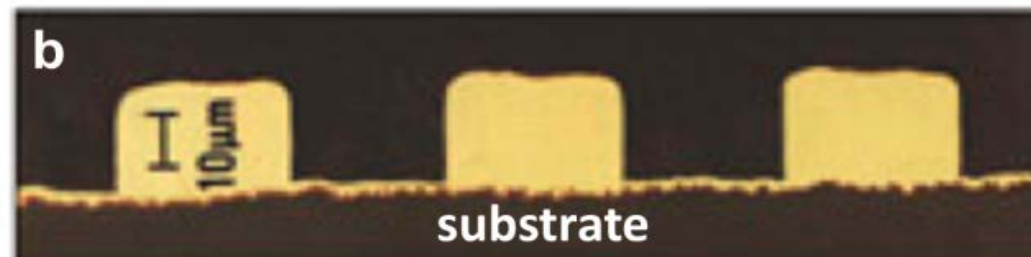
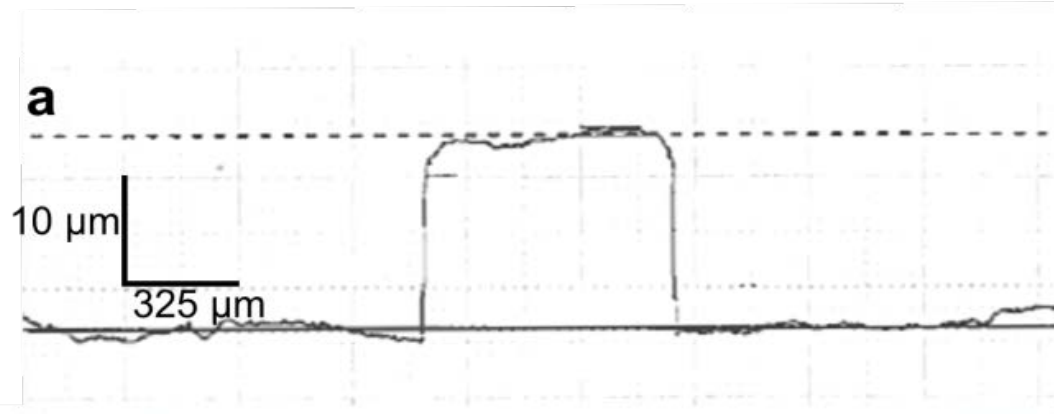
Plated and Etched Sample

- Panels were subjected to standard pattern plating process to produce circuitry and peel test coupons
- Pre-Clean, Dry Film Lamination, Image, Develop, Pattern plate, Tin Plate, Film Strip, Etch, Tin Strip



Etching Results

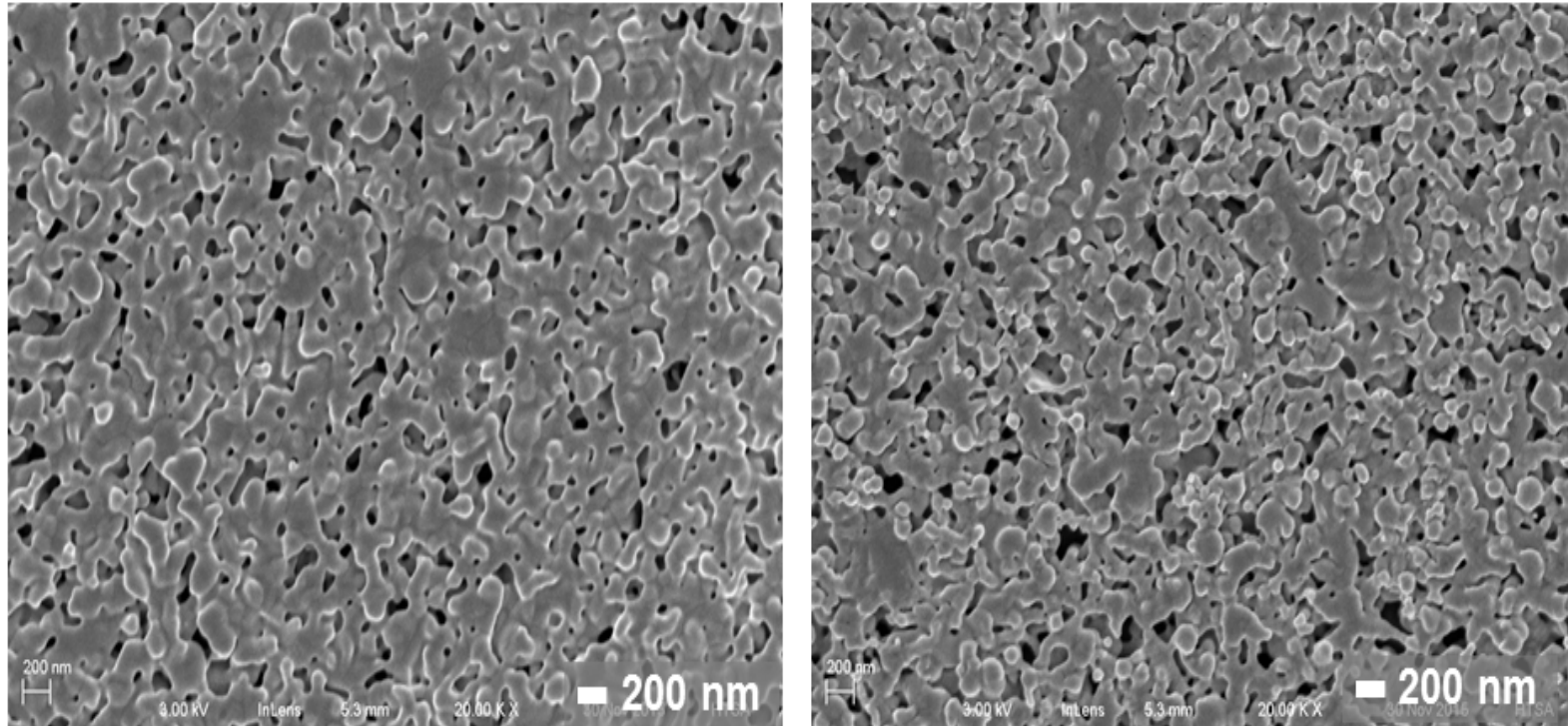
- Etch results were excellent
- Very straight side walls due to very thin base copper to be etched.
- Profilometry graph and cross section pictures show very straight side walls.
- Very important for high speed and RF Designs.



Other Results

- ASTM Tape test of sintered copper was 5B
- Peel strength of finished traces were below 1 N/cm in most cases. This is unacceptable.
- Experiments were designed to determine the loss of adhesion during processing.

Sintering Study



The flash lamp used in the lab is a single unit and caused banding of the sintered copper. The SEMs above show well sintered copper on the left and over sintered copper on the right. The right image was captured from the over lap area of the sintering flashes

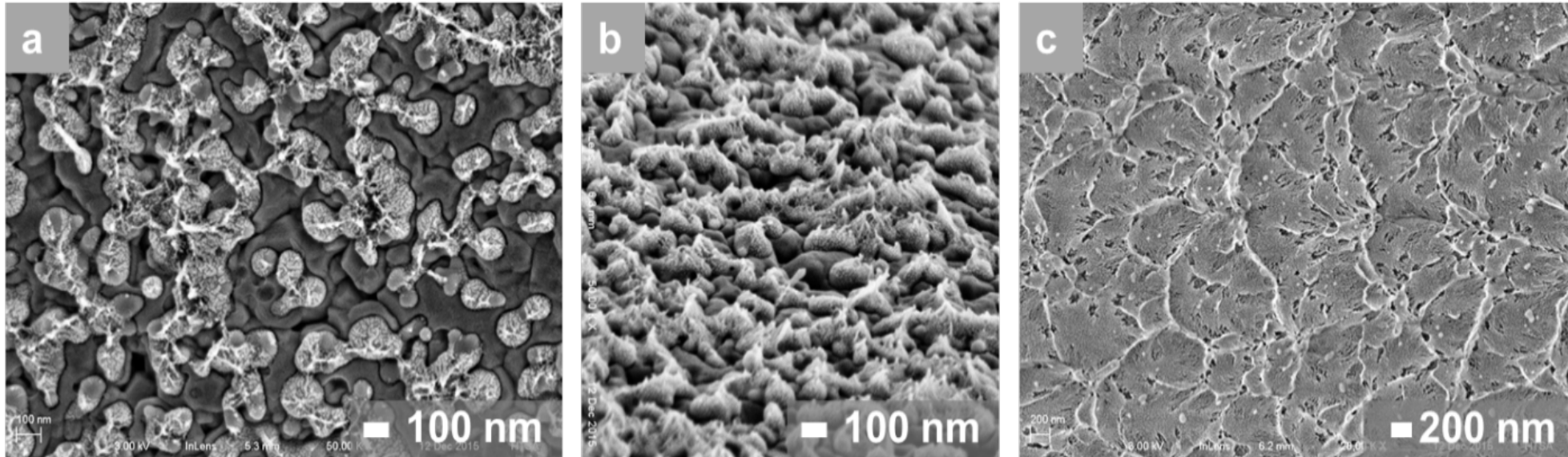
Better Sintering

- Uneven sintering caused variability in adhesion.
- This was fixed by flash lamp vendor with a roll to roll conveyORIZED multi lamp unit with PLC control.
- This provided even sintering.

More Consistency

- Peel Strength more consistent but still not acceptable.
- More SEM pictures were made.
- Pictures showed that residual binders needed to be present after sintering to provide acceptable adhesion.

SEM Shows Binders



SEM images of gold sputtered samples of a sintered and plated copper film, peeled from the substrate. (a) Top view of the peeled film. (b) Tilted view of the peeled film. (c) Top view of the substrate underneath.

Binder Study

- Differences in adhesion can be traced to residual binders shown on SEM images.
- The Binder also seemed to be affected by plating and etching chemistries.
- Multiple binders were evaluated with multiple solvent systems.
- Chosen for resistance to aqueous chemistry and acids.

A List of Binders / Solvents

- Binder / Solvent combination needs to provide a stable dispersion of the Nano Copper.
- 5 Combinations seemed to be stable

Dispersant	Solvent	Stable ink
Polyvinylpyrrolidone	DEGBE	Yes
Polyoxyethylene octyl phenyl ether	EG/1M2P	No
Polyvinylpyrrolidone-polyvinylacetate copolymer	EG/1M2P	No
Polyvinylpyrrolidone-polyvinylacetate copolymer	DEGBE	No
Polypropylene carbonate	propylene carbonate	No
Polypropylene carbonate	N-methyl-2-pyrrolidone	No
Polypropylene carbonate	DEGMEEA	No
Hyperdispersant A	DEGMEEA	No
Hyperdispersant A	DEGBE	Yes
Polyvinyl butyral	DEGBE/MMB	Yes
Dispersant B	DEGBE	No
Polyether polyamide	DEGBE	No
Polyalkyleneoxy terminated polyamide	DEGBE	No
Polymethacrylate copolymer	DEGBE	Yes
Polymethacrylate copolymer	DEGBE/butanone	Yes

Repeat the PCB Fabrication Process

- Flexible Polyimide was Meyer bar coated, dried, sintered, and sent to fabrication.
- Several formulations showed improved adhesion.

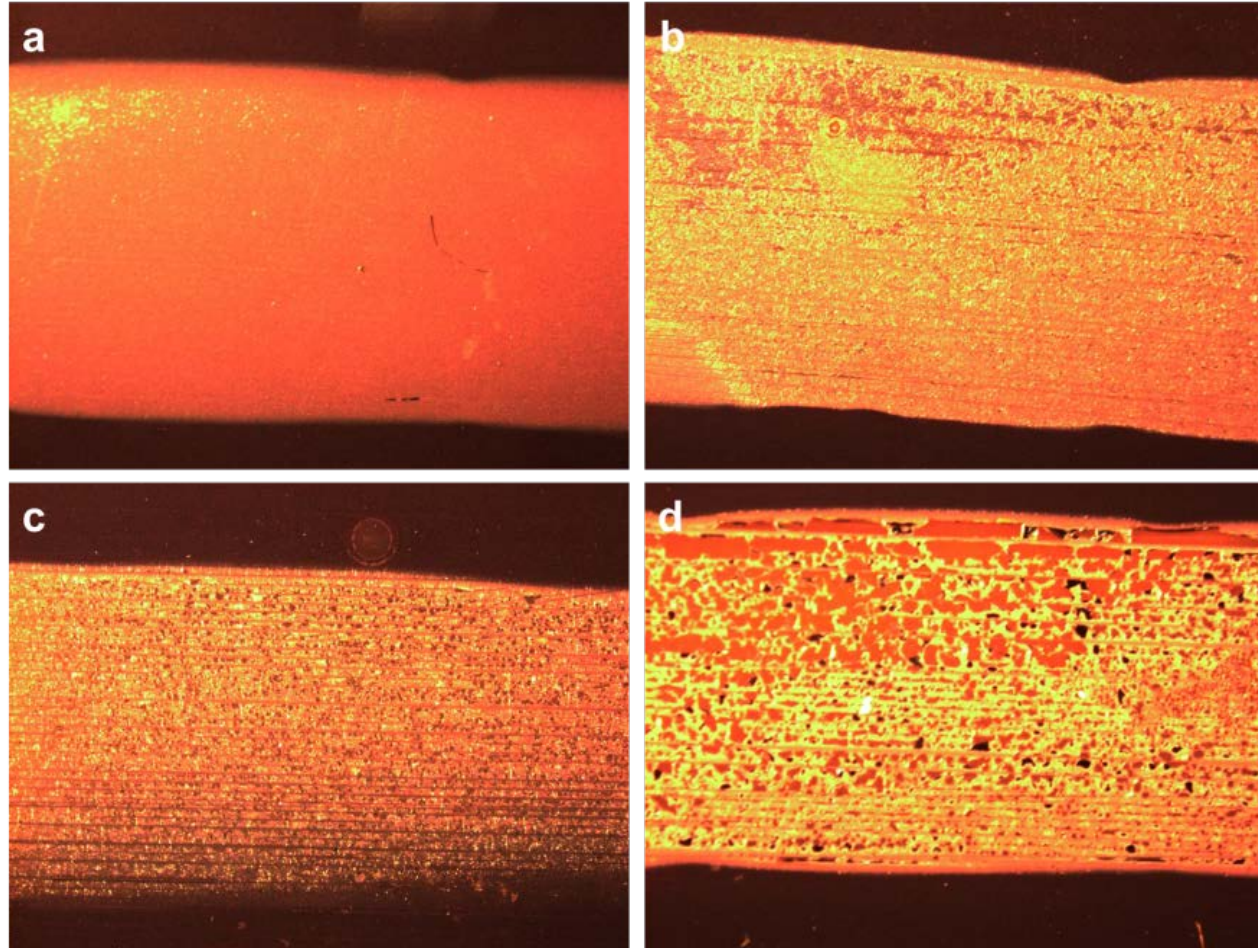
Dispersant	Solvent	Max. peel strength (N/cm)		
		1	2	3
Polyvinylpyrrolidone	DEGBE	4.4	4.4	---
Hyperdispersant A	DEGBE	6.8	0	4.5
Polyvinyl butyral	DEGBE/MMB	0	0	---
Polymethacrylate copolymer	DEGBE	8.0	3.8	3.4
Polymethacrylate copolymer	DEGBE/butanone	0	0	---

Surface Treatments

- Published literature points to Plasma and sputtered metals to promote adhesion on Flexible substrates.
- Plasma Treatment did NOT improve adhesion.
- Metallic coatings prevented the even application of the Nano Copper Ink.
- Potassium Hydroxide treatment is planned as well.

Surface Treatments

- . Micrographs of coated nano copper films on
- (a) plasma treated PI;
- (b) PI with 5-7.5 nm of chromium coating;
- (c) PI with 7.5 nm of titanium coating and
- (d) PI with 7.5 nm of chromium/100 nm of copper coating.



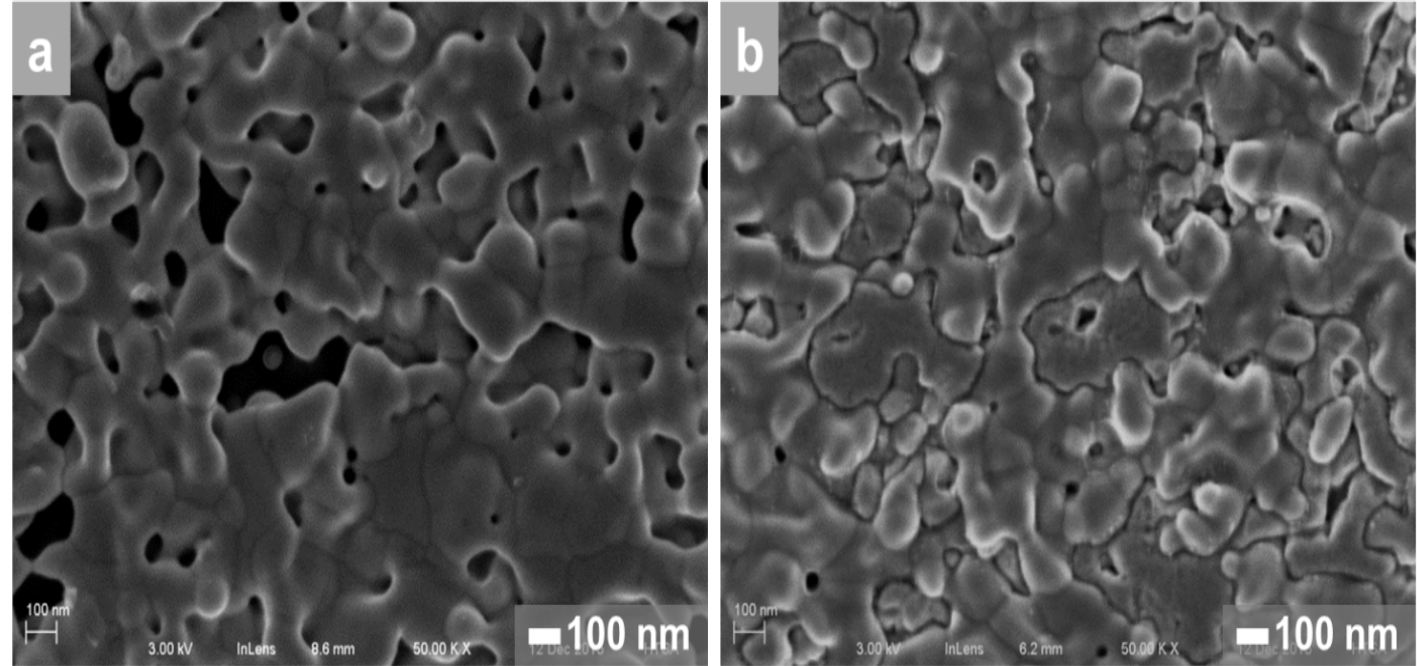
Other Options

- Several types of flexible polyimide were tried, including one pre-treated by the manufacturer to enhance the adhesion of metallic coatings.
- The vendor modified substrate did show some signs of improved adhesion.

Polyimide	Max. peel strength (N/cm)		
	1	2	3
Regular	4.4	4.4	---
Modified	4.8	5.6	5.1

Copper Plating

- Copper plating penetrates into the Nano pores and spaces between the sintered particles.
- This makes for excellent adhesion of the plated copper to the base copper.
- This penetration may have an effect on adhesion.



SEM images of (a) a sintered nano copper coating and (b) the substrate facing side of the same coating after plated to $\sim 5 \mu\text{m}$.

What was learned

- The sintered Nano Copper Ink has excellent adhesion to flexible polyimide (5B)
- The adhesion suffers after standard PCB processing.
- The adhesion is affected by both sintering energy and binder chemistry.
- The ultra thin copper foil is able to be processed with standard PCB techniques.
- The ultra thin copper allows for much improved etch resolution over standard foil thicknesses.

More Findings

- Nano copper thin film technology appears to be a viable, low cost way to get base copper thicknesses that were only possible by Plasma Deposition equipment.

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- Brett Austin and the staff at Nationwide Circuits for their work plating and etching samples
- Prof Mark Poliks and his students at Binghamton University for conducting the metal sputtering work