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Laser Printing Circuit Boards and Electronics

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Abstract. *Although significant progress has been made toward digital printing of electronics using inkjet technologies, the potential of laser printing for digital fabrication has been largely overlooked. Despite their speed and resolution capabilities toner-based systems are often regarded as incapable of handling conductive materials. This research reports recent laser printing development and its potential to replace conventional printed circuit board manufacturing steps, including conductive track deposition. The research had a dual focus, demonstrating proof of concept with conventional office laser printers (for artwork masks, etch resists, and seed layers for overplating), and used industrial laser printers with developmental toners to support direct production of electronics (conductive tracks, dielectric layers, and legends). The results confirm that laser printing can complement other digital printing approaches for directly depositing resists and conductive tracks. © 2012 Society for Imaging Science and Technology.*
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INTRODUCTION

Conventional printed circuit board (PCB) production is capital equipment, water, and energy intensive, and uses a selection of hazardous chemicals which are difficult and costly to dispose of. Current PCB production methods have been optimized to produce maximum integrity conductive "tracks", normally in copper, by first cladding the entire surface of laminate board by electrodeposition and then chemically etching away the majority of the metal coating except in masked areas where the tracks are needed to connect components.

Significant research efforts have demonstrated the potential for digital printing technologies to reduce the time, cost, energy and chemicals required for PCB production. Development work to replace subtractive etching processes with direct deposition of conductive tracks has received much attention and is currently dominated by "wet" inkjet approaches (actuated by piezo, thermal, or aerosol) that are largely predicated on the use of conductive metal nanoparticles suspended in a carrier liquid.[1–5] Inkjet is currently the forerunner in this area because it provides an efficient non-contact mask-free pattern deposition method using off the shelf print heads capable of depositing a wide variety of ink formulations.[6] Inkjet technologies have also been introduced commercially to streamline conventional etch-based manufacturing steps, for example the recently launched etch resist printing system Lunaris by Mutrac^x (an Océ spinoff). As this technology matures, industrial interest and acceptance of digital electronics printing will continue to increase.

While the merits of inkjet approaches are well documented and have paved the way into many PCB applications, inkjet technologies can suffer from head reliability problems, inconsistencies in droplet formation, inks which are not waterfast, difficulty depositing high dielectric constant layers, substrate wetting challenges and relatively low deposition efficiency for solid content (typically <25 vol.%) in the carrier liquid.[7–9]

These shortcomings in combination with the increased interest for digital workflow provide an opportunity for other digital print technologies such as electrophotography (EP), the basis of laser printing, to be considered for electronics applications.[10] Although EP requires significant investment (for toner and fuser development), its unique technical strengths and the anticipated demand for PCB and other digital fabrication applications justifies further investment in this technology.

The potential to use electrophotography for circuit manufacture was first considered in the mid-1950s when an employee of Haloid (later Xerox), Frederick A. Schwertz, was tasked with looking at special applications for the technology.[11] Since that time other researchers have recognized the potential of printing toner with high speed and resolution for electronics applications.[12–14] Laser printing is capable of printing a variety of materials, including polymers, ceramics

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Table I. Conventional PCB process steps.

1.	**Produce artwork masks**
2.	Drill substrate for through hole components
3.	**Produce conductive tracks via etching**
4.	**Flood print solder resist**
5.	**Flood print circuit reference legend**
6.	Apply finish to pads via hot air solder leveling
7.	CNC route the final board shape
8.	Populate and finish board

Bold = steps targeted for optimization in this research.

and metals, offering the potential to support a wide range of PCB manufacturing steps.[14–18] Furthermore, office-based laser printing is inherently waterfast and produces thicker layer deposition (typically 5 μm) than comparable inkjet printing.

This research, undertaken with two industrial partners, considered the feasibility of using laser printing to replace conventional PCB manufacturing steps. The research had a dual focus and is therefore written in two parts. First, proof of concept and immediate implementation of conventional office laser printers to streamline prototype PCB production was explored (for mask generation, directly printed etch resists, and seed layers for overplating). Second, the use of industrial laser printers and developmental toners to support direct printing of electronics (conductive tracks, dielectric layers, and circuit reference legends) was investigated. The results help to debunk the myth that EP systems cannot handle conductive toner and promise a future for EP in digital fabrication.

OVERVIEW OF CURRENT PCB PROCESS STEPS

Conventional PCB production process steps have been documented elsewhere and vary in sequence from manufacture to manufacturer and even from job to job depending on accuracy requirements. The majority of the workflow at the industrial collaborators involves rigid and flexible double-sided, through hole plated and multilayer PCBs; however, proof of concept for this project was based on single-sided boards. A typical high value single-sided PCB manufacturing process flow at Quartz Technical Services Ltd (Quartz TSL), UK, is shown in Table I.

The process steps which were substituted or simplified using laser printing as part of this investigation are shown in bold in Table I and will be discussed individually.

EP PRINTING SYSTEMS, TONER, AND PCB MATERIALS

Unless otherwise specified, the rigid substrates used in these trials were 1 ounce (∼35 μm thick) copper-clad FR-4 glass-reinforced epoxy laminate board (Kingboard Laminates Ltd, Hong Kong) and the flexible substrates were 1 ounce (∼35 μm thick) copper-clad flexible polyimide film (Kapton®, supplied via Merlin Flex-Ability Ltd, UK).

Printing for all developmental toners and rigid substrates was done using a two-component printer (Monochrome 1, CTG PrintTEC GmbH, Germany) designed for tile decoration. Flexible substrates were printed onto using a variety of office-based printers with manufacturer's standard black toner.

PROCESS SUBSTITUTIONS

Produce artwork masks

A key process in conventional PCB manufacture is the production of ultraviolet (UV) opaque artwork masks, used in downstream process steps for selective curing of materials via exposure to UV radiation. The state of the art method for producing artwork masks in high accuracy (up to 50,800 dpi) is laser plotting of chemically treated film, which is currently supplied via a subcontractor to both industrial partners. In order to streamline PCB prototype production and introduce the industrial partners to the benefits of digital printing, masks were printed using standard office laser printers and their effectiveness was evaluated against conventional laser plotted artwork. This was the first experience with laser printed artwork for both commercial partners.

A typical circuit pattern was printed in single and double layers (two printing passes) onto translucent artwork film (Laserstar, Mega Electronics Inc., NJ, USA) using office laser printers (HP LaserJet 4, 1200, and 4200n, Hewlett-Packard, USA and AcuLaser C2800, Epson, Japan). The artwork density was evaluated visually using a light box and fully backlit optical microscope (Leica DM4000m, Leica Microsystems GmbH, Germany). The artwork was also used to produce an etch resist from UV-sensitive dry film resist (KP-2100 Series, Kolon, Korea) laminated onto copper-clad board and a solder resist from flood printed UV ink (OPSR-5600/J-GS10, ELGA, Italy). A 15 s exposure with 8 light units at 2 kW lamp setting was used for the etch resist and a 40 s exposure with 35 light units at 3 kW was used for the solder mask (using a Cirgraphics 3000 exposure unit, Cirgraphics Ltd, UK).

Optical evaluation for samples revealed acceptable UV opacity for thin lines (using visible light transmission as a proxy for UV), but unacceptable levels of light transmission for large areas. For example, the mask produced by the HP 4200n had the poorest performance with a light transmission of 14 ± 1.14% in large areas and resulted in a solid 3 on a standard 21-step transmission step wedge compared with the laser plotted artwork which had a transmission of 0% and a solid 9 (out of 21) step wedge reading. When a laser printed artwork (single pass, LaserJet 1200) was used to make an etch resist, undesired cross-linking of the dry film resist due to overexposure (excess UV transmission) occurred, as shown in Figure 1.

Figure 2 compares the resulting PCB where the etch resist and solder resists were produced from masks made by laser plotting (left) and single-layer laser printing (using PCB settings in the AcuLaser C2800 printer driver) (right). This detail image shows the most challenging portion of the test PCB produced, where a high density of fine surface mount

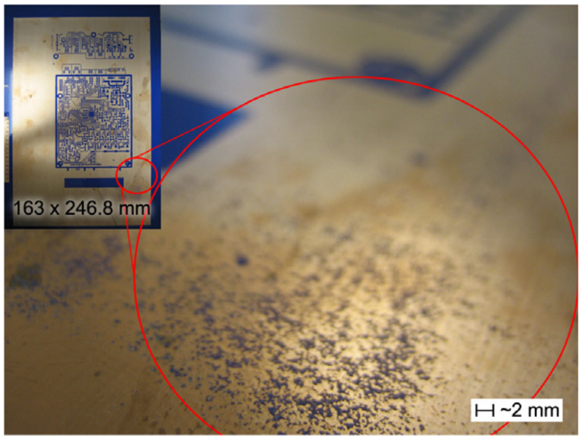

Figure 1. Etch resist defects in large areas from overexposure through a single-layer laser printed artwork.

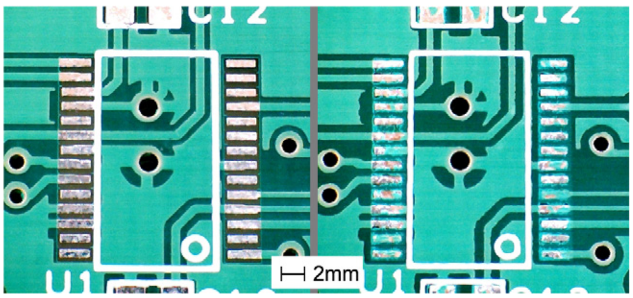

Figure 2. Detail of a PCB board produced from laser plotted artwork (left) and single-layer laser printed artwork (right).

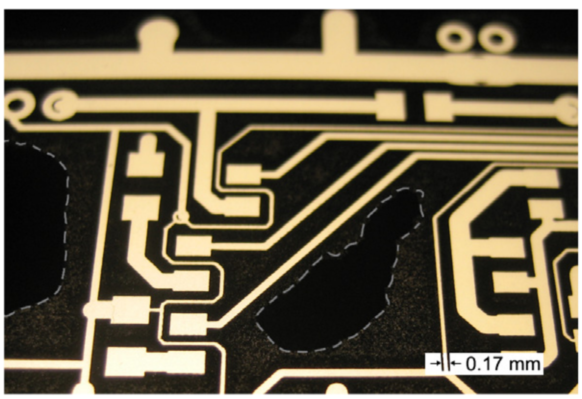

Figure 3. Laser printed artwork with double printed areas (in dashed lines) to compensate for low density in large areas.

lands for an integrated chip were required. The laser plotted artwork delivered PCB layers at the expected standard of accuracy and alignment, while the layers produced from the laser printed masks suffered from poor edge definition of the solder resist around the individual lands and inferior alignment.

Due to defects arising from single-layer high resolution masks, the large areas were subsequently double printed (Figure 3), which improved the density of the masks; for example, the mask from the HP 1200 improved to 0.6 ± 0.11% with a solid 6 (out of 21) step wedge reading, which is marginally acceptable for prototype production.

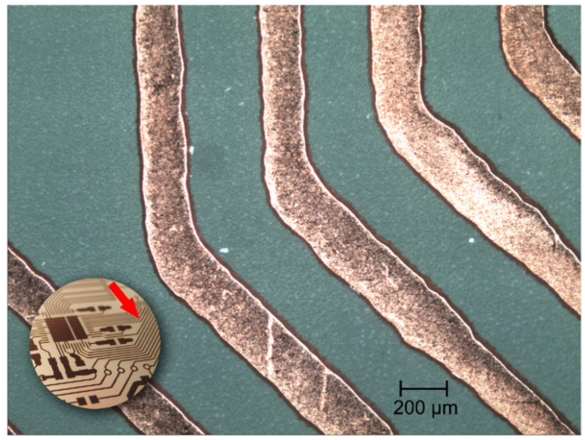

Figure 4. Copper tracks etched using a laser printed mask with double printed areas.

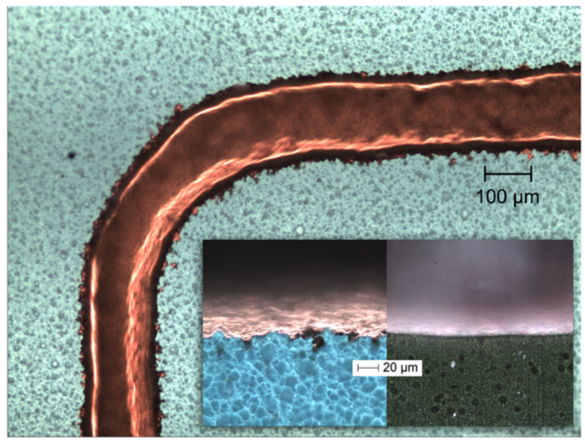

Figure 5. Detail of tracks edges etched using a laser printed mask on rigid (main image and left inset) and flexible (right inset) substrates.

The etch resist double printed as shown in Fig. 3 enabled the production of the conductive tracks in Figures 4 and 5 which did not exhibit defects due to excessive UV transmission on any part of the board.

The process conveniently produced tracks designed to be 170 µm wide (with 250 µm pitch spacing); however, variation in the width was evident (Fig. 4). Furthermore, the tracks produced on the rigid substrate exhibited ragged edges (Fig. 5), while tracks produced in the same way on the flexible substrates were smoother (see right inset image in Fig. 5). It was difficult to obtain line widths of less than 100 µm even when using printers with 600 dpi (42 µm) resolution or higher.

Although laser printing artwork may be regarded as best suited to hobbyists, it reveals inherent strengths and weaknesses in the laser printing process. For example, although tracks were easily produced on both rigid and flexible substrates, the line edges were not sharp on the rigid board, perhaps due to influence from the texture of the board (Fig. 5). Furthermore, developing tracks which are wider than the area exposed to light in the charge-generation layer of the OPC is a well-known phenomenon and could be improved by optimizing the printers and toner to the application including the use of advanced thin single-layer photoreceptors (such as high gamma photoconductors which have been shown to improve sharpness and resolution).[19,20] The line width limits demonstrated here (without any optimization to the printers/toner) achieved results on a par with prior investigations.[14] Also, the poor deposition density in large areas is a known issue for laser printing which was solved for printing images on paper many years ago, but which may need to be readdressed for digital fabrication applications.[21] Arguably the process delivers its best performance where it is needed most because, due to the fringe field effects, the thickest layer deposition is where fine lines are printed, making the UV transmission lower per layer printed where the circuitry is the most dense.[22] The older the laser printer used to print the masks the less UV transmission. This could be attributed to the resolution of the printer and particle size of the toner, where the older printers used a larger toner size which resulted in thicker printed layers imparting better UV blocking characteristics. This being the case implies tension between the need for higher resolution (requiring smaller toner) and sufficient mask density requirements (requiring larger toner).

Despite the resolution and quality limitations, laser printed artwork can be produced rapidly in house using latent capacity on conventional laser printers with no additional capital equipment expense. For these reasons, both industrial partners have benefited by adopting this method to produce artwork in house for iterative prototyping of a surprisingly large proportion of PCB designs. In order to assure quality, once the board design has been finalized, conventional artwork is used in production.

Produce conductive tracks

Although recent research has made significant progress toward directly deposited conductive tracks, the cost, conductivity and mechanical integrity of electrodeposited copper still generally offer one or more orders of magnitude superiority in each of those characteristics.[23] For most circuitry applications these advantages oblige continued use of etching processes in the near term. The substeps for etching away unneeded copper at Quartz TSL are shown in Table II, and they require an etch mask, which can easily be applied with appropriate feature definition, is chemically resistant and mechanically stable during the etching step, and then can be easily stripped off afterward.

(a) First, an artwork mask is produced for the etch resist; (b) next, the entire copper-clad side of the PCB is laminated with dry film resist; (c) next, the PCB is exposed to UV radiation through a mask in order to cross-link the film which will form the etch mask; (d) the PCB then goes through a weak film stripper in order to slough off the film which was not cross-linked; (e) next, it goes through the etcher in order to remove unneeded copper; (f) after that, the PCB goes through the film stripper to remove the cross-linked etch mask; (g) finally, the oxidation is cleaned off of the copper tracks via brushing. These substeps are time-consuming, complicated and are associated with significant financial and environmental costs. An effective digital printing step could eliminate the need for the etch resist mask and replace substeps (a)–(d) for indirectly produced tracks or (a)–(f) for directly deposited conductive tracks.

Table II. Substeps to conventionally etch away unneeded copper.

3.	**Etch away unneeded copper (substeps)**
(a)	Produce artwork mask
(b)	Laminate copper-clad substrate with UV-sensitive dry film resist
(c)	UV expose film through mask of tracks
(d)	Remove underexposed film (masked areas) via a weak film stripper
(e)	Etch away unneeded copper via chemical bath
(f)	Remove the hardened etch mask via a stripper
(g)	Clean oxidation from copper tracks via brushing

Conductive tracks via etching (through directly printed resists). Capitalizing on the inherent waterfast nature of EP, the use of office-based laser printing was evaluated for the direct printing of etch resist patterns onto flexible copper-clad polyimide substrates. The flexible substrates were cut into strips (40 × 100 mm) and an abrasive cleaner followed by isopropanol alcohol (IPA) were applied to the copper side to remove any oxidization and clean the surface. The strips were then bonded onto A4 sheets of paper and a series of lines (with a thickness of 0.25 mm, 1.075 mm, 1.5 mm and 2.4 mm) was printed directly onto the copper using an office printer (LaserJet 1300, Hewlett-Packard, CA, USA). Several methods were trialled to effectively fuse the toner onto the copper including the printer's heated roller. Samples were also fused using a short-wave (1–3 μm) 12 kW infrared heater (Solar H2, Infra-Red Systems Co., UK) with exposure times from 10 to 80 s at full power with a 200 mm standoff distance and a lab-scale oven (MCP Ltd, UK) with thermostat control set to 60, 80, and 100°C (monitored by the thermocouple to +5°C) with fusing times from 1 up to 10 min. Once fused, samples were tested for adhesion to the substrate using sticky tape, and if the toner was not sufficiently attached, the samples were discarded. The chemical resistance of the printed toners was evaluated on an etching line (Advanced Systems Inc., USA) with a speed of 37 (factory standard for 1 ounce cladding ∼1 min duration) using alkaline ammoniacal etchant (Centurion Speciality Chemicals, UK). Further down the line, the samples were stripped using an aqueous concentrated organic alkaline stripper (Aquastrip 1330, BLT Circuit Services Ltd., UK); stripping the resist was also done through manual application of isopropanol alcohol (IPA) and propylene glycol phenyl ether (PGPE). Samples were inspected visually and using reflected light optical microscopy (Leica DM4000m, Leica Microsystems GmbH, Germany).

During printing, a portion of the toner back transferred onto the fuser roller rather than the copper substrate and it was prone to jamming; these issues ultimately required the removal of the fuser unit and exploration of alternative fusing

Table III. Results from oven fusing trials.

Duration (min)	60°C	80°C	100°C
1	X	X	X
2	X	X	+
3	X	X	+
4	X	+	++
5	○	+	++
7	○	+	+++
10	○	++	+++

X = failed adhesion test; ○ = did not survive etcher; + = degree of fusing.

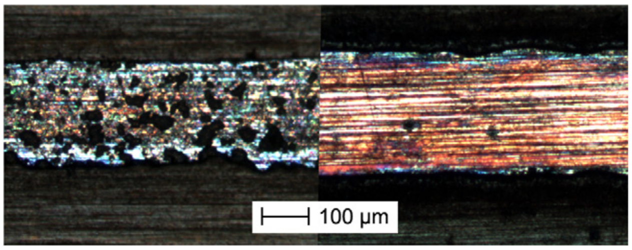

Figure 6. Optical microscopy of 0.25 mm copper tracks produced via etching through directly printed toner etch resists oven fused for 4 min (left) and 10 min (right).

methods reported in more detail below. Once fully fused into a contiguous layer, the toner proved an effective resist with ample chemical resistance to the ammoniacal etchant. However, the fused toner etch resist proved very difficult to strip using the standard stripper (Aquastrip 1330). Even after two passes through the stripper portion of the line, evidence of toner removal was difficult to ascertain. Manually rubbing the toner with IPA was also ineffective; but PGPE was found to remove the toner without affecting the copper tracks. Samples which were fused at lower temperatures wiped clean with very light agitation, while more cohesively fused toner (60°C and up) was softened by soaking for 1 min in PGPE and then wiped clean using little effort.

Fusing trials demonstrated infrared to be a faster and more thorough toner fusing method than the oven. All samples fused by infrared for more than 30 s passed the adhesion test and went down the etching line. The fusing results from the oven trials were more variable and are reported in Table III. Less-well-fused toner failed the adhesion test and even some samples which did were not sufficiently bonded to survive conditions in the etcher.

Figure 6 shows tracks with an 0.25 mm design width as protected from etchant by etch resists directly laser printed with toner and oven fused at 100°C for 4 min (left) and 10 min (right). Samples fused for 4 min scarcely survived the etching process and resulted in tracks with severe defects, while samples fused for 10 min only had very minor defects by comparison. The tracks produced in each case were undersized.

Figure 7 shows tracks with an 0.25 mm design width as produced using directly printed toner etch resists fused with

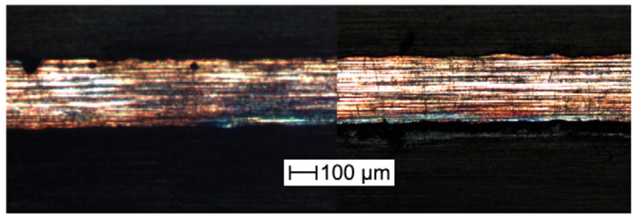

Figure 7. Optical microscopy of 0.25 mm copper tracks produced via etching through directly printed toner etch resists fused by infrared for 70 s (left) and 80 s (right).

infrared for 70 s (left) and 80 s (right). Samples fused for 70 s exhibited minor defects in the conductive tracks, while samples fused for 80 s exhibited higher integrity. The tracks produced were also undersize.

As shown by comparing the left-hand and right-hand sides of Figs. 6 and 7, both oven and infrared heating methods show a clear trend that adhesion to the substrate increased with increased fusing time and temperature. This can be explained by the increased degree of particle melt and coalescence which reduced the etch resist porosity and thereby improved the quality of the resulting tracks. Where there was a contiguous layer of fused toner the copper was protected and vice versa. The fact that resists oven fused at 60°C were washed away during the etching process was evidence that the fusing temperature was not high enough to promote sufficient toner coalescence and adhesion to the substrate.

Comparatively, from the figures it can be seen that the edge definition is not as sharp as those produced using a traditional etch resist. There are a number of reasons for this. First, the resolution of the directly printed etch resist was limited by the 1300 dpi LaserJet 1300 printer resolution (which actually develops tracks at a lower resolution as discussed in section headed *Produce artwork masks*) whereas the laser plotted artwork had a resolution of 4000 dpi. Also, a conventional etch resist is made from a laminated dry film which is already a contiguous layer and is therefore less susceptible to defects than relying on discrete toner particles consolidating and leveling into a contiguous layer. Furthermore, the toner deposited was extremely brittle in nature. The pressure of the etchant spray could have dislodged or aggravated minor defects to result in removal of toner at the edge. This may explain why the direct printed etch resists had a tendency to produce track widths which were undersized. It should also be noted that as the line thickness increased so too did the porosity. This could be another manifestation of the fringe field effects which lead to reduced toner deposition in the middle of larger areas as discussed previously in the section headed *Produce artwork masks*.[24]

These trials illustrate that the inherent print thickness and waterfast nature of office printed toner can be exploited for producing chemically resistant etch resists, although the office printer fuser struggled adhering toner onto copper-clad substrates. Analysis of all the fused samples illustrated the fusing effectiveness imparted by infrared presented not only the least porous mask but also the most durable. In order to consider laser printing as a viable direct etch production method, significant future work is required to develop efficient fusing means and investigate implications of changing the toner material and/or stripping solution/means for PCB materials.

Conductive tracks via seed layer deposition and plating. Several researchers have explored EP as a means of indirectly producing conductive layers.[25] Aoki et al. have demonstrated the potential to laser print a seed layer for subsequent electroless overplating where the toner used was produced by mixing resin with up to 70 wt.% fine copper particles and then grinding.[12] Furthermore, the potential to plate seed layers which have conductivities as low as 1/50th that of the bulk metal has been discussed.[26] Aimed at prototype production, a trial was undertaken to explore whether conventional black magnetic toner had sufficient conductivity (imparted by the iron oxide and carbon black content) to act as a seed layer for subsequent electrolytic plating.

Seed layers in the form of circuitry tracks were printed and fused onto flexible polymer acetate sheets using conventional standard black magnetic toner and an office printer (LaserJet 1200, Hewlett-Packard, CA, USA). The seed layers were then attached to a voltage source to act as the cathode and submerged into a tank of copper sulfate dissolved into diluted sulfuric acid (1 part acid to 3 parts water). Direct current was applied through a copper anode in the tank. Samples were dipped for 10 min durations at 1, 2, 3, and 6 A. For some samples the duration at 3 A was extended up to 20 min. Following removal from the tank the seed layers were rinsed with deionized water.

Unfortunately there was no evidence of metal plating on any of the samples. Presumably, this is due to insufficient conductivity of the toner (due to the relatively low concentrations of iron oxide and carbon black) and lack of metal at the surface to act as seed catalyst. Further bespoke toner development has not been considered for this step due to success in the direct laser printing of conductive tracks reported below.

Conductive tracks via direct deposition. Directly deposited conductive tracks by digital printing methods eliminate the need for global electrodeposition of copper (or other conductives) onto substrates along with any downstream etching processes. This represents the most elegant solution for minimizing waste to produce conductive tracks in PCB production. It has been investigated via a variety of approaches, including laser direct writing,[27] laser micro-cladding,[28] and ink and aerosol jetting of conductive nanoinks.[1–5] This section begins the second part of the article, which is focused on direct additive manufacture of PCB layers using industrial laser printers (from CTG PrintTEC GmbH) and specialized toner.

The fundamental challenge for EP-based approaches lies in the fact that the toner must contain conductive material in order to form conductive tracks, but must not

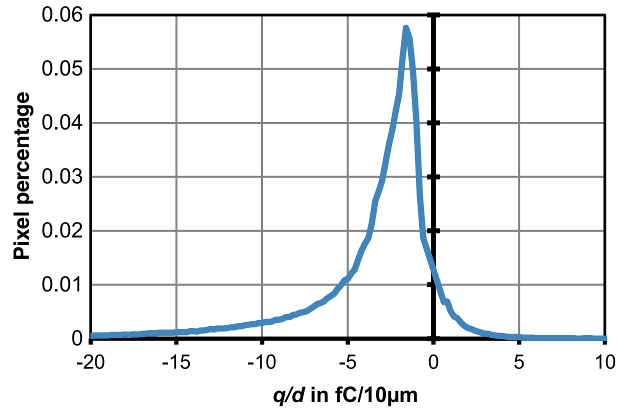

Figure 8. Charge distribution of silver particle-based toner.

be conductive during (electromagnetic brush) development inside the printer. Past research aimed at EP-based conductive toner deposition either failed[28] or lacked evidence of substantive development (beyond theoretical or early feasibility studies).[29]

Over the past three years, a method[30] has been refined to coat silver particles with polymer as a pretreatment enabling production of toner particles which act like an insulator inside the printer and then can be consolidated into conductive tracks after printing onto ceramic substrates by post-firing (results for co-firing the tracks and substrates[31] and laser melting conductive tracks in situ[28] are reported elsewhere).[15] The most recent work has investigated the effect of the shape of silver (flakes versus spherical particles) used in the toner on the printability, conductivity, and integrity of the tracks.[31]

In order to make this comparison, two toners with identical formulations were prepared except one used silver particles (spherical) and the other silver flakes. The weight percentage of silver in both toners was identical, and both shapes of silver received the same third-generation pretreatment. When paired with an appropriate carrier, the charge distribution for the silver particle-based toner (Figure 8) had a mean charge to particle diameter ratio q/d of -5.0 fC/10 µm with between 1.7 and 3.3% of positively charged particles, and the silver flake-based toner (Figure 9) had a mean q/d value of -4.5 fC/10 µm and 5.2% of positively charged particles (measured using a q/d meter[32], EPPING GmbH, Germany).

Up to ten layers of toner were then printed in 0.2, 0.5, and 1.0 mm width tracks onto fired ceramic substrates using a two-component printer (Monochrome 1, CTG PrintTEC GmbH, Germany). The tapes were fired with the following heat profile: 5°C/min heating rate up to 875°C, a 15 min dwell at that temperature, followed by a cool down at the same rate. A second round of trials was undertaken in which a single layer of toner was printed onto fired substrates which had been pretreated with a sodium chloride-based brine solution (CTG PrintTEC GmbH, Germany) intended to improve the substrate chargeability (thus enhancing transfer efficiency) with the same firing regime.

As an example of the tests performed, the failure rate and mean sheet resistance (calculated from six samples) of 0.5

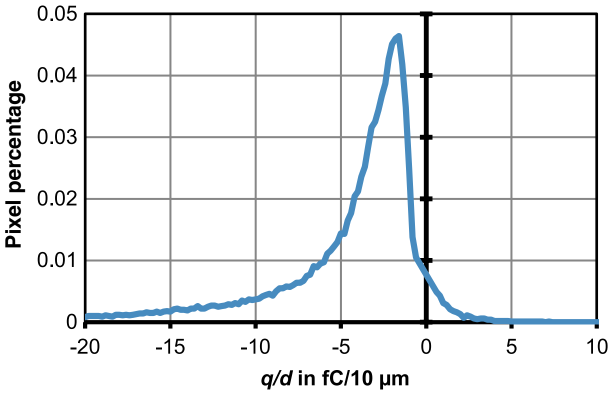

Figure 9. Charge distribution of silver flake-based toner.

Table IV. Failure rate and mean sheet resistance of post-fired silver lines (0.5 mm width, $n = 6$) from particle-based and flake-based toners.

No. of toner layers	Particle-based		Flake-based	
	Failure rate (%)	R_{sq} (Ω)	Failure rate (%)	R_{sq} (Ω)
1	100	N/A	100	N/A
2	50	45.2	100	N/A
3	0	10.5	67	20.0
4	0	8.6	17	20.8
5	0	5.7	33	11.9
6	0	6.9	67	13.2
7	0	5.3	17	9.4
8	0	5.0	17	8.7
9	0	3.7	100	N/A
10	0	3.9	0	6.9

mm lines resulting from the initial round of trials are shown in Table IV.

The particle-based toner had no failed tracks when printed with three to ten toner layers and showed a clear trend of reduced mean sheet resistance with increasing number of layers down to ~4 Ω. The flake-based toner suffered from higher failure rates due to transverse crack formation in the tracks, but also showed a trend of reduced mean sheet resistance down to ~7 Ω.

The flake-based toner suffered frequent and unpredictable track failure and was less conductive than the particle-based toner, which performed more reliably. Even if the total failure of all samples and with nine layers is considered an outlier due to external circumstance (like a printer failure or an operator's error), such a failure never occurred with particle-based toners in these or prior trials. Inspection of the silver lines (Figure 10b) shows the problems of the flake-based toner which are inhomogeneous and suffer from broken lines. Obviously, the silver flakes do not adhere to each other very well, nor do they adhere to the substrate as desired. This indicates higher vulnerability of the flake-based silver lines to defects. These results corroborate previous experiments with silver flake-based toner which yielded inconsistent performance due to transverse cracking (which were not reduced with a higher firing temperature).[30]

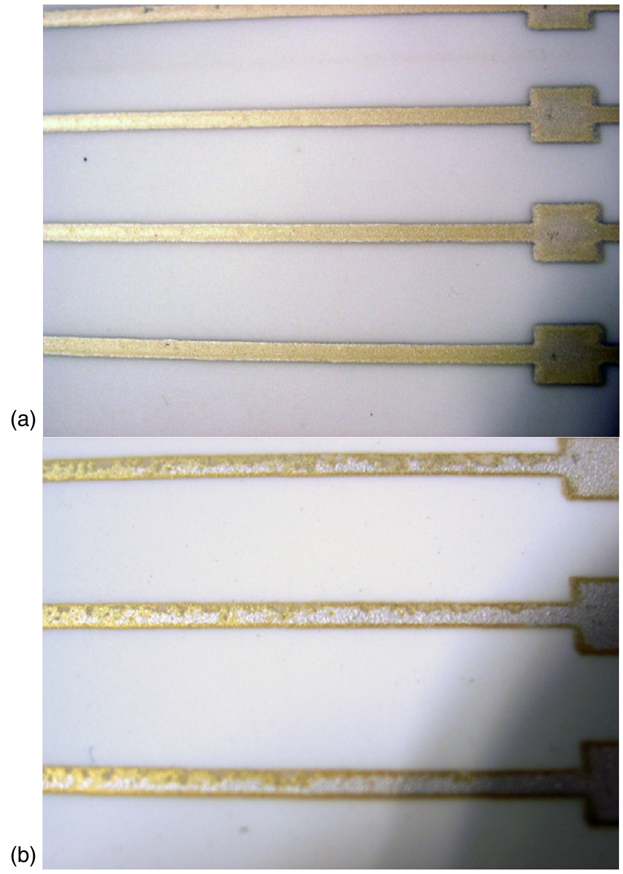

Figure 10. Post-fired silver lines (nominal line width 1.0 mm) produced from six layers of particle-based (a) and seven layers of flake-based toner (b).

Table V. Failure rate and mean sheet resistance of single-layer post-fired silver lines on surface-treated ceramic.

Line width (mm)	Particle-based		Flake-based	
	Failure rate (%)	R_{sq} (Ω)	Failure rate (%)	R_{sq} (Ω)
1.00	0	41.8	17	51.5
0.50	50	38.1	0	38.9
0.20	83	72.3	83	68.5

The second round of trials on brine-treated substrates yielded a nominal 20% increase in toner deposition by weight and resulted in failure rate and mean sheet resistance as shown in Table V.

Both types of toner experienced improved transfer efficiency using the brine treatment; however, it is unclear if the electrical properties of the brine or the tacky residue it left on the ceramic, or a combination of the two, contributed to the improvement. The particle-based toner printed lines (Figure 11a) were better shaped and denser than flake-based toner lines, although the difference in quality was not as big as expected.

Figure 11. Post-fired silver lines produced from single layers of particle-based (a) and flake-based (b) toner on surface-treated ceramic.

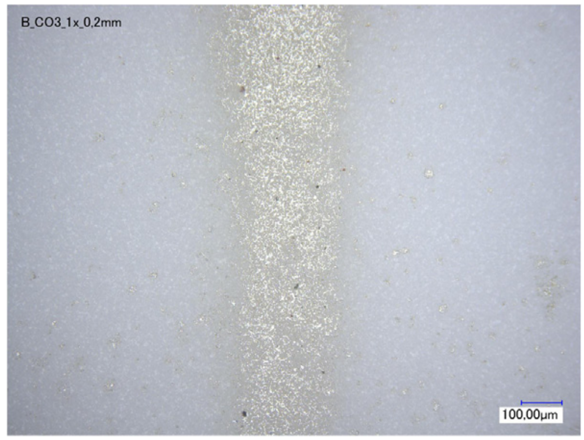

Figure 12. Post-fired silver line produced from a single layer of particle-based toner with a 200 µm width.

In contrast to the first round of trials, tracks produced by the flake-based toner with 0.5 mm width had a failure rate of 0 %. Compared to the other lines, the flake-based toner lines (Fig. 11b) demonstrated weaker density and obvious defects which account for the lower conductivity; however, the line is well shaped with sufficient density to provide a measure of conductivity. In addition to the samples shown above, the treatment enabled single-pass printing down to a nominal 200 µm track width (Figure 12) with a sheet resistance of 72.3 Ω. Attempts to print narrower lines experienced limits akin to the office-based printers/conventional toners in the section headed *Produce artwork masks*; however, this is an encouraging result given the lack of printer optimization. Although the conductivity and failure rate are not yet satisfactory, the improvements made by applying surface treatment enabled electrophotographically printed conductive silver lines to be produced with only one layer of toner for the first time. This is a major achievement for EP.

The comparison between conductive tracks laser printed from particle and flake-based conductive silver toners shows that spherical silver particles yield more conductive and reliable silver lines than flake-based toners developed to date. Furthermore, feasibility of conductivity after a single printing pass has been proven. These results can be considered a decisive step toward utilizing the full potential of EP (regarding resolution, accuracy and print speed) in digital fabrication of thick-film electronics.

Despite the progress demonstrated, further development is necessary. The single-layer line density needs to be improved and the transfer process and firing regime need to be optimized. Also, the surprisingly strong performance of single-layer flake-based toners requires further investigation and may lead to a new approach toward toner based on flake-shaped silver. Lastly, these results justify additional toner and printer refinement (including high-resolution photoreceptors) as discussed earlier to enable realization of narrower lines with improved optical density and conductivity.

Solder resist and legend printing

Although the direct production of insulating layers and solder resists in particular has been discussed by several researchers,[33–35] it has received considerably less attention than the direct deposition of conductive materials. Once the conductive tracks have been produced (regardless of whether they were additively or subtractively made), a solder resist is needed to protect against the possibility of solder bridging between tracks during the application of solder to exposed pads or surface mount bonding lands. The key requirement for the solder resist is sufficient thermal stability to survive in downstream process steps including hot air solder leveling (HALS) and solder baths.

For accuracy requirements, silk screen printing of the circuit reference legend at Quartz TSL has been superseded with the same lithography process and materials used for the solder resist (but in a different color). Furthermore, the legend printing immediately follows the application of the solder resist, which thereby imposes the same thermal stability requirements for legends. For these reasons, evaluation of the developmental solder resist toners was also undertaken for direct legend printing to provide an alternative to direct legend printing via inkjet deposition of UV-curable inks.[33]

Directly printed solder resists and legends have the potential to simplify the PCB production flow at Quartz

Table VI. Substeps to flood print protective resist.

4./5. Flood printing solder resist and legend (substeps)	
(a)	Produce artwork mask
(b)	Flood print the entire area with UV-sensitive ink
(c)	Partial bake (for 20 min @ 75°C) to solidify ink
(d)	UV expose required pattern through a mask
(e)	Remove the underexposed ink (on the pads, etc.) via a weak film stripper
(f)	*Repeat* steps (a)–(e) for circuit reference legend
(g)	Bake solder resist and legend (for 60 min @ 150°C)

TSL which prior to this research followed these substeps to produce the solder resist and legends (Table VI).

(a) First, an artwork mask is produced for the solder resist; (b) next, the entire copper-clad side of the PCB is flood printed with UV-curable ink; (c) the entire PCB is baked in an oven for 25 min at 75°C in order to solidify the ink; (d) next, the PCB is exposed to UV radiation through a mask in order to cross-link the ink which will form the solder mask; (e) finally, the PCB goes through a weak film stripper in order to slough off the ink over the pads which was not cross-linked. In order to achieve full strength, the protective resist requires further baking which is deferred until after steps (a)–(e) are repeated for the circuit reference legend which is printed directly on top of the solder resist. After the solder resist and legend have been deposited, the board is baked for 60 min at 150°C in order to impart full strength and thermal resistance to the deposited material. The substeps in Table VI are complicated, costly, and could be eliminated with an effective two-pass digital printing step (one pass for the solder resist and one for the legend).

Two epoxy-based toners were prepared as candidates for solder resist and legend printing. The first was a thermosetting epoxy resin with a high softening temperature T_g and cross-linking temperature (~160–180°C), which, when paired with an appropriate carrier, had a charge distribution (Figure 13) with a mean q/d value of -2.83 fC/10 μm and between 3.1 and 2.2% of positively charged particles (measured using a q/d meter, EPPING GmbH, Germany).

A second UV curing epoxy toner was prepared via mixing and mechanical grinding (ZEAC, Switzerland). The toner incorporated yellow pigment and two photoinitiators (Irgacure 819 and 2559, BASF, Germany), and when paired with a carrier exhibited similar charge distribution as shown in Fig. 13. The UV-curable toner had a lower initial fusing temperature (90–110°C), which offered advantages over thermosetting epoxy.

A series of standardized test patterns was printed onto copper-clad FR-4 glass-reinforced epoxy board and flexible polyimide film. In order to evaluate their suitability for solder resists and legend printing, patterns were printed onto bare substrates, copper, and baked flood printed green UV ink (Figure 14). Once printed, all samples were fused via a medium-wave (3–25 μm) 12 kW infrared heater (Flare FSMw, Infra-Red Systems Co., UK) which was built into the industrial laser printing rig[36] and samples with UV activated

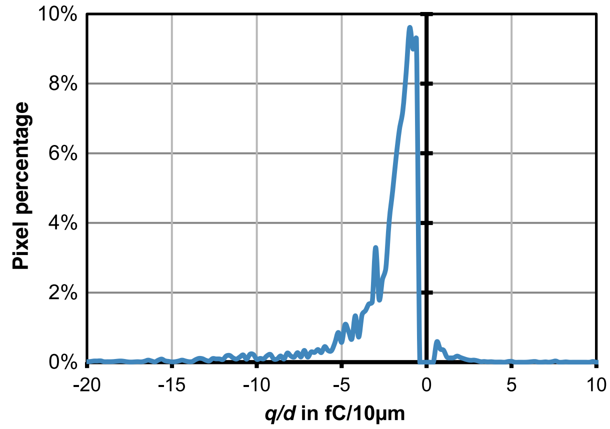

Figure 13. Charge distribution of thermosetting epoxy toner.

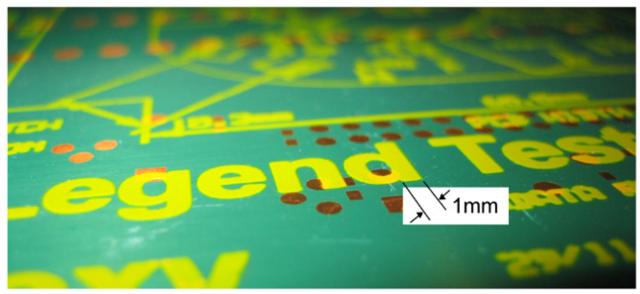

Figure 14. UV-cured epoxy toner printed on top of conventional solder resist and exposed copper areas of a rigid glass-reinforced board.

toner were cured via a 40 s exposure with 35 light units at 3 kW (Cirgraphics 3000, Cirgraphics Ltd, UK). Once printed and cross-linked, the samples were run through downstream processes including hot air solder leveling (Lantronix B.V., Netherlands) for a 7 s surface treatment cycle, a conventional flow solder machine (CMS 400 converted to lead-free temperatures, Blundell, UK) moving over a 270°C solder bath at 1 m/min, and an ROHS-compliant infrared surface mount oven with eight heat zones (LFR400 Tornado, ADTEC Convection Technology, UK) for ~6 min at 285°C.

The toners were deposited by laser printing onto rigid (Fig. 14) and flexible substrates (Figure 15). The 1.6 mm thickness of the rigid laminate resulted in a relatively weak field strength for conventional transfer, so a heat and pressure transfer was used. When printing directly onto copper it was necessary to ensure the copper was isolated from ground in order to avoid sparking and some imperfections in the image were noticeable (note the letter "g" in Fig. 15).

During sample evaluation in the hot air solder leveling process (Figure 16a), the thermal shock experienced during the standard treatment length of 7 s (at 270°C) caused toner to run on all the samples printed using UV-cured epoxy toner (Fig. 16b). Less severe but similar shortcomings were observed when cycled for only 3 and 1 s. The thermosetting epoxy toner performed without any notable degradation.

Despite the poor performance in the hot air solder leveling process, the UV-curable toner was stable on the

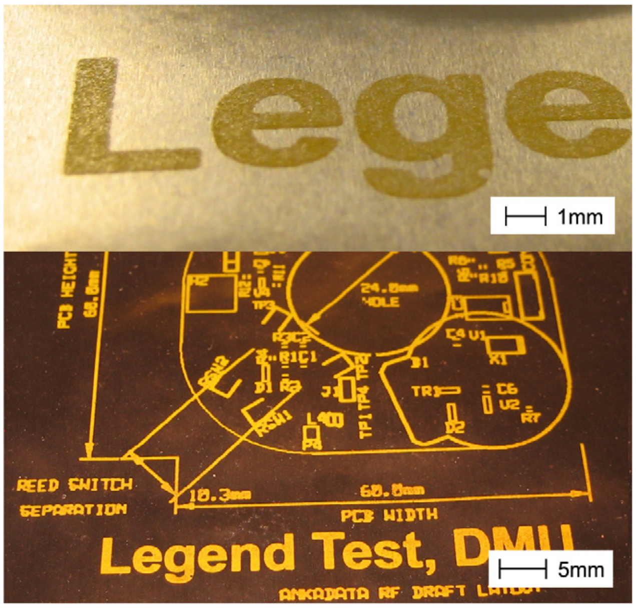

Figure 15. UV-cured epoxy toner printed on top of copper-clad polyimide film.

(a)
(b)

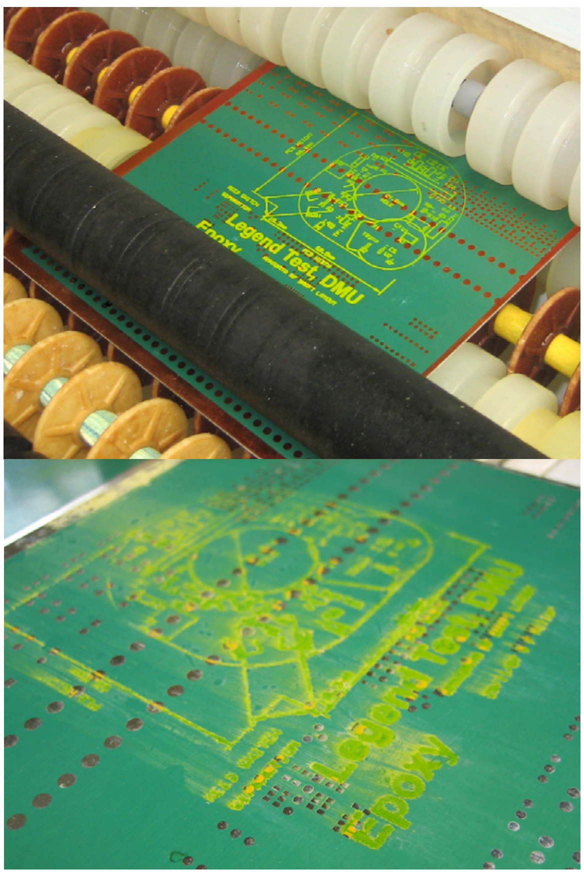

Figure 16. Legend/resist trial with UV-cured epoxy toner before (a) and after (b) passing through the hot air solder leveler.

through flow solder line and in the surface mount oven. Evaluation after the through flow solder line demonstrated good adhesion to the substrate and resistance to scratching, even though the surface became slightly tacky. Evaluation following the surface mount oven showed a difficult to scratch off layer with much better adhesion to the substrate and no tackiness. The thermosetting epoxy toner had suitable thermal stability for all of the downstream processes.

Table VII. Digital PCB process steps with conventional board assembly.

~~**1.**~~	~~**Produce artwork masks**~~
2.	Drill substrate for through hole components
3.	**Produce conductive tracks via ~~etching~~ *direct deposition***
4.	**~~Flood~~ *Digitally* print solder resist**
5.	**~~Flood~~ *Digitally* print circuit reference legend**
6.	Apply finish to pads via hot air solder leveling
7.	CNC route the final board shape
8.	Populate and finish board

Italics = new steps; ~~strikethrough~~ = eliminated steps.

Although the thermosetting epoxy toner demonstrated stronger performance, the speed and cost advantages for the lower-temperature fusing requirements make implementation of the UV-curable epoxy toner more desirable. The poor performance of the UV-curable toner in the hot air solder leveling process and tacky surface after exposure to molten solder (on the flow solder machine) indicate that it did not fully cross-link during the early thermal fusing step and subsequent UV exposure. Further investigation of the metal halide lamp in the UV exposure unit revealed a spectral distribution which included a peak at 360 nm, which corresponds to the wavelength needed for deep curing Irgacure 819, but it did not have a peak at 280 nm, which is the wavelength required for surface curing Irgacure 2559. Without both required wavelengths, it is likely that the UV-curable toner was never fully cross-linked, which would explain its poor thermal stability. Its improved performance in the surface mount oven may have resulted from better cross-linking due to the additional exposure to infrared radiation (in the oven).

The potential for using epoxy-based toners to directly laser print solder resists and legends has been demonstrated. Furthermore, the selective deposition capabilities of digital printing removes the need for UV curing because there is no step involving exposure through a mask; however, the potential to fuse toner at a lower temperature and higher speed provides continued impetus for development of UV-curable toners. The shortcomings identified in the curing process open up the possibility for continued toner and curing development. Additional work is also required to improve the resolution, which currently enables minimum line widths between 100 and 200 μm.

CONCLUSIONS

This feasibility study has demonstrated the potential to eliminate step number 1 and substantially streamline steps 3–5 (Table VII) in the current production flow at the industrial partners using various embodiments of laser printing.

Although further work is required for implementation of laser printing at any of the steps in Table VII, the inherent strengths of laser printing have been highlighted, and they offer the possibility to complement and compensate for shortcomings in other digital deposition/fabrication approaches. Most important, this research highlights progress in the direct deposition of conductive tracks which negates what is often a perceived weakness of EP for printing electronics. The flexibility of toner formulation to adapt to different requirements in the PCB process has also been demonstrated. The production of PCBs is a foundation step toward integrated direct deposition of passive and active components and eventually the substrates and packaging as well.

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REFERENCES

[1] J. Perelaer, C. E. Hendriks, A. W. M. de Laat, and U. S. Schubert, "One-step inkjet printing of conductive silver tracks on polymer substrates," Nanotechnology **20**, 165303 (2009).

[2] K. Woo, D. Kim, J. S. Kim, S. Lim, and J. Moon, "Ink-jet printing of Cu–Ag-based highly conductive tracks on a transparent substrate," Langmuir **25**, 429–433 (2008).

[3] D. Kim and J. Moon, "Highly conductive ink jet printed films of nanosilver particles for printable electronics," Electrochem. Solid-State Lett. **8**, J30–J33 (2005).

[4] A. Sridhar, D. J. van Dijk, and R. Akkerman, "Inkjet printing and adhesion characterisation of conductive tracks on a commercial printed circuit board material," Thin Solid Films **517**, 4633–4637 (2009).

[5] H. M. Nur, J. H. Song, J. R. G. Evans, and M. J. Edirisinghe, "Ink-jet printing of gold conductive tracks," J. Mater. Sci.: Mater. Electron. **13**, 213–219 (2002).

[6] A. Khan, K. Rahman, M.-T. Hyun, D.-S. Kim, and K.-H. Choi, "Multi-nozzle electrohydrodynamic inkjet printing of silver colloidal solution for the fabrication of electrically functional microstructures," Appl. Phys. A: Mater. Sci. Process. **104**, 1113–1120 (2011).

[7] P. Calvert, "Inkjet printing for materials and devices," Chem. Mater. **13**, 3299–3305 (2001).

[8] E. Özkol, J. Ebert, K. Uibel, A. M. Wätjen, and R. Telle, "Development of high solid content aqueous 3Y-TZP suspensions for direct inkjet printing using a thermal inkjet printer," J. Eur. Ceram. Soc. **29**, 403–409 (2009).

[9] B. Derby, "Inkjet printing ceramics: From drops to solid," J. Eur. Ceram. Soc. **31**, 2543–2550 (2011).

[10] D. Büttner, W Diel, and K Krüger, "Digital printing of conductive silver lines: comparison between inkjet and laser printing," *Proc. 12th Eur. Ceram. Soc. Conf.* (European Ceramic Society, Stockholm, Sweden, 2011).

[11] D. Owen, *Copies in Seconds: How a Lone Inventor and an Unknown Company Created the Biggest Communications Breakthrough Since Gutenberg: Chester Carlson and the Birth of the Xerox Machine*, (Simon & Schuster Paperbacks, New York, 2004).

[12] H. Aoki, N. Yamaguchi, C. Takubo, K. Imamiya, T. Yamauchi, and H. Hashizume, "A study of electrophotography process for manufacturing printed circuit board," *Proc. IS&T's NIP20* (IS&T, Springfield, VA, 2004) pp. 241–245.

[13] A. Iida, K. Ishii, Y. Shinjo, H. Yagi, and M. Hosoya, "Digital fabrication using high-resolution liquid toner electrophotography," J. Imaging Sci. Technol. **51**, 465–472 (2007).

[14] A. Walker and D. F. Baldwin, "Initial investigations into low-cost ultra-fine pitch solder printing process based on innovative laser printing technology," IEEE Trans. Electron. Packag. Manuf. **22**, 303–307 (1999).

[15] D. Büttner, K. Krüger, A. Schönberger, D. Jung, and B. Zobrist, "Laser printing of conductive silver lines," *Proc. IS&T's NIP26 and Digital Fabrication 2010* (IS&T, Springfield, VA, 2010) pp. 139–142.

[16] A. Kumar Das, "An investigation on the printing of metal and polymer powders using electrophotographic solid freeform fabrication," (University of Florida, Gainsville, Florida, 2004) p. 177.

[17] K. M. Boivie, R. Karlsen, and C. Van der Eijk, "Material issues of the metal printing process, MPP," *Proc. 17th Solid Freeform Fabrication Symposium* (University of Texas, Austin, USA, 2006).

[18] N. J. Manjooran, A. Kumar, and W. M. Sigmund, "Development of a liquid toner for electro-photographic solid freeform fabrication," J. Eur. Ceram. Soc. **26**, 2459–2465 (2006).

[19] K. Seino, H. Hirahara, T. Konuma, I. Yoshida, and S. Kaieda, "Photoinduced and dark discharge mechanisms of high gamma photoreceptors," J. Imaging Sci. **54**, 60502-1–60502-9 (2010).

[20] D. S. Weiss and M. Abkowitz, "Advances in organic photoconductor technology," Chem. Rev. **110**, 479–526 (2009).

[21] ASTM, $F2036\text{–}05^{\varepsilon 1}$ *Standard Test Method for Evaluation of Larger Area Density and Background on Electrophotographic Printers*, (ASTM International, West Conshohocken, PA, USA, 2009).

[22] J. E. Fay Jr., *Electrostatic Analysis of and Improvements to Electrophotographic Solid Freeform Fabrication*, (University of Florida, Gainsville, Florida, 2003) pp. 110.

[23] J. Perelaer, P. J. Smith, D. Mager, D. Soltman, S. K. Volkman, V. Subramanian, J. G. Korvink, and U. S. Schubert, "Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic materials," J. Mater. Chem. **20**, 8446–8453 (2010).

[24] S. S. Raut, *Investigation of Layer Thickness Uniformity of Laser Printing*, (De Montfort University, Leicester, UK, 2009).

[25] P. S. Sherman, "Direct production of conductive/resistive traces on a flexible substrate using a computer/printer system," *Proc. IEEE's Industry Applications Conference/ 30th IAS Annual Meeting* (IEEE, 1995) Vol. 2, pp. 1817–1821.

[26] B.-G. Lee, "Fabrication of micro-conductive patterns on glass surfaces using a laser direct writing method," J. Ceram. Process. Res. **10**, 729–738 (2009).

[27] X. Li, X. Zeng, H. Li, and X. Qi, "Laser direct fabrication of silver conductors on glass boards," Thin Solid Films **483**, 270–275 (2005).

[28] J. B. Jones, D. I. Wimpenny, R. Chudasama, and G. J. Gibbons, "Printed circuit boards by selective deposition and processing," *Proc. 22nd Solid Freeform Fabrication Symposium* (University of Texas, Austin, TX, USA, 2011) pp. 639–656.

[29] C. Wagner, R. Patwardhan, B. Jang, and M. Mahinfalah, "Electrophotographic direct-write for electronics," *Proc. NSTI Nanotechnology Conference and Trade Show* (2006) pp. 206–209.

[30] D. Büttner, W. Diel, and K. Krüger, "Pre-Treatment of silver particles as a basis for functional toner," *Proc. IS&T's NIP27 and Digital Fabrication 2011* (IS&T, Springfield, VA, 2011) pp. 462–465.

[31] D. Büttner and K. Krüger, "Improving performance of laser-printed conductive silver lines," *Proc. IMAPS/ACerS 8th International Conf. on Ceramic Interconnect and Ceramic Microsystems Technologies* (IMAPS/ACerS, Erfurt, Germany, 2012).

[32] A. Küttner and R. H. Epping, "Theory and practice of a small toner-charge-spectrometer," *Proc. IS&T's NIP14* (IS&T, Springfield, VA, 1998) pp. 623–626.

[33] K. Clay, I. Gardner, E. Bresler, M. Seal, and S. Speakman, "Direct legend printing (DLP) on printed circuit boards using piezoelectric inkjet technology," Circuit World **28**, 24–31 (2002).

[34] H. Gleskova and S. Wagner, "Electrophotographically printed insulator," Mater. Lett. **52**, 150–153 (2002).

[35] T. Sutter, "An overview of digital printing for advanced interconnect applications," Circuit World **31**, 4–9 (2005).

[36] J. B. Jones, D. I. Wimpenny, G. J. Gibbons, and C. Sutcliffe, "Additive manufacturing by electrophotography: challenges and successes," *Proc. IS&T's NIP26 and Digital Fabrication 2010* (IS&T, Springfield, VA, 2010) pp. 549–553.