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Precision Rolled-Ink Nano-Technology; Development of a Direct Write Technique for the Fabrication of Thin Films and Conductive Elements

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14. ABSTRACT
Direct-writing offers serial or point deposition for the fabrication of two-dimensional linear elements or patterns. A common use for direct write technologies in two-dimensions is the fabrication of sensors, antennas and other conductive circuitry. This article describes the development of a novel, low-cost technique for the direct deposition of conductive elements on multiple substrates. Precision Rolled Ink-Nanoparticle Technology (PRINT), described here, is used to deposit particulate solutions, termed “inks” in order to create the conductive elements. The utility of PRINT is shown for multiple substrates with varying surface topographies, including: fiber reinforced polymer composites, glass, metals, ceramics, and others. Development of the PRINT system and future work are discussed.

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direct write, direct deposit, micro-composite, thin film, conductive ink

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1. Introduction

Direct writing is an additive manufacturing practice that is generally used for the deposition of particulate solutions (solute dissolved or dispersed in a solvent) or liquids, which are termed inks. Inks are limited by processing temperatures and viscosities compatible with the processing equipment. The deposited inks are used to create thin films, electronic elements, functional surfaces, or structural patterns without the use of masks or etching processes. Subsequent heat treatments are often employed in order for the deposited material to achieve maximum performance. Many of the direct write technologies currently available commercially were originally designed to perform specific research functions, and their current processing parameters and capabilities reflect their initial intent. Some limitations include: ink viscosity, particle loading, particle size, ambient conditions, orientation of the deposition tool to the substrate, and others. Most direct write techniques are designed for deposition onto flat substrates, and require a particular stand-off distance between the deposition head and the substrate.

One current research program at the U.S. Army Research Laboratory (ARL) requires the deposition of identical and continuous conductive elements on multiple substrates with varying topographies. This project also requires the deposition of both commercial and in-house formulated inks. It was determined that there was not a commercially available technology suitable for this program, which led to the development of Precision Rolled Ink-Nanoparticle Technology (PRINT). Background information on various direct write technologies is presented along with the development and application of PRINT.

2. Background

There are many direct write technologies available today, however, Zhang, et al. (*1*) has suggested that four major categories exist, including: (1) droplet-based, (2) filament-based, which is sometimes referred to as a continuous approach or flow-based technique, (3) tip based, and (4) laser based direct writing. For this article, I have added a fifth category; direct penning. (*1–5*)

Aerosol Jet[*] and Inkjet printing are common droplet-based techniques, which eject inks on to the desired substrate. Aerosol Jet uses aerosolized inks that are deposited through a deposition head via high pressure sheath gas. A comprehensive description of this process can be seen in references *6* and *7*. Aerosol Jet is a non-contact printing method that has a variable stand-off

[*] Aerosol Jet is a registered trademark of Optomec, Inc.

distance of 1 to 5 mm, which provides for the ability to deposit continuous features on morphologically uneven surfaces, within the processing stand-off distance. However, this system is limited in that the ink to be deposited must be able to be aerosolized into droplet sizes between 1–5µm. This, along with the diameter of the jet orifices, therefore defines the particle size limiting factor and the deposition capabilities of the technology, which are line widths of 5–150 µm. (*1, 6, 7*).

Inkjet printing is generally separated into two drop-on-demand (DOD) technologies: thermal DOD inkjet and piezoelectric DOD inkjet. Thermal DOD inkjet technology is typical of consumer office printers that deposit water-based pigments or dyes, but are rarely used in direct writing. Piezoelectric DOD inkjet deposits a fixed amount of ink that is ejected through a nozzle using a piezoelectric action. The ink is held in a chamber that is contracted and expanded through a controlled external voltage. The sudden contraction of the chamber creates a shockwave in the ink, which causes the ink to exit the nozzle. A comprehensive description of the piezoelectric DOD inkjet technology can be seen in references *8* and *9*. The ejected ink droplet then falls, via gravity onto the substrate and then dries through solvent evaporation. Deposited features are defined by many variables, including: nozzle orifice diameter, droplet volume, ink viscosity, ink particle loading, ink-substrate compatibility, surface tension, and others. Piezoelectric DOD inkjet printing is also restricted in that the nozzle tip must be kept at a consistent distance from the substrate, which makes the technology difficult to use with morphologically non-uniform surfaces. (*1, 8–9*).

MicroPen[†] and nScrypt are filament-based, non-contact direct write techniques, which deposit materials continuously instead of as droplets. The MicroPen technology stores material in a syringe, which is connected to the deposition head of the system. A pneumatic ram forces material from the syringe to the deposition head and pressurized to up to 14 MPa (2000 psi) and dispensed through the writing tip. The technology is described in detail in reference *10*. The MicroPen can be used to deposit materials with a viscosity range of 0.005 to 500 Pa·s, making for a large library of materials that can be processed with this technology. The MicroPen requires a multi-axis table to ensure that the tip remains perpendicular, and at a defined distance, to the substrate. (*10*)

nScrypt also uses high pressure to dispense materials with their SmartPump[‡] technology. Pneumatic pressure and accurately controlled valves maintain the desired material flow and resulting deposition. This technology is described in reference *11*. The nScrypt SmartPump dispense materials with a viscosity range of 0.001 to 1000 Pa·s, making the system one of the most versatile technologies available. This technology also makes use of a pressure differential within the tip in order to provide absolute control of the stopping and starting of deposition. This delivers consistent flow negating agglomeration and maintaining feature definition at the ends of

[†] MicroPen is a registered trademark of MicroPen Technologies Corporation.

[‡] SmartPump is a trademark of nScrypt, Inc.

lines or elements. Like MicroPen, the nScrypt technology also requires a multi-axis table to ensure that the tip remains perpendicular to the substrate and at a defined distance from the substrate. (*1*, *11*)

Dip-pen nanolithography (DPN), and polymer pen lithography (PPL) are tip-based direct writing techniques, which use capillary effect to deposit inks. DPN is the only direct write technique that has precision on the molecular level, which allows for deposition features in the sub 100 nm range. DPN was developed by Piner, et al., (*12*) during research into condensation issues of water on the tip of an atomic force microscope (AFM). DPN uses the condensation that can form on an AFM tip to transport molecular inks to the surface of the substrate. A variation of DPN called thermal dip pen nanolithography (tDPN) adds a heating element to the AFM tip allowing for the deposition of melted materials instead of water-based inks. DPN and tDPN provide for fine features at high precision; however, these techniques are slow and therefore low through-put processes. These techniques are also make use of an AFM cantilevered arm and are not viable for direct writing on the micro scale.

The deposition process for PPL is much the same as DPN, with the transfer of inks from a fine tip. PPL, however, uses elastomeric tips that are not mounted on cantilevers like traditional AFM tips. PPL tips are also generally mounted in an array in order to increase the amount of ink that can be deposited at one time. PPL is also not viable for direct writing on the micro scale. (*13*)

There are many uses for lasers in lithographic processing that are subtractive in nature, particularly the use of laser machining for processing lithographic masks. Examples can be seen in references *14–17*. As for additive processes, there are four major types of processing technologies: (1) laser induced forward transfer (LIFT), (2) Matrix Assisted Pulsed Laser Evaporation Direct Write (MAPLE DW), laser-guided direct write (LGDW), and flow-guided direct write (FGDW). LIFT and MAPLE DW both use rely on the pixilated transfer of thin film ribbons onto a receiving substrate. LGDW and FRDW use aerosolized inks that are deposited via momentum transfer from optical and/or hydrodynamic forces. In LGDW, the aerosol and laser are transmitted through a hollow optical fiber and are focused onto the substrate for deposition. FRDW uses gas flow and multiple orifices to create streams of aerosol that are projected on the substrate with the aid of the laser beam. These laser direct write techniques are generally used for deposition on uniform, flat surfaces, and require specific stand-off distances. Laser direct write systems are also costly due to the lack of commercially available turn-key systems (*1, 2, 18*).

Conductive penning was not directly developed as a direct write technique. Initial application of conductive pens was for quick circuit repair. There are commercially available conductive pens, like, CircuitWorks[§] from ITW Chemtronics, which come loaded with a conductive silver ink that

[§] CircuitWorks is a registered trademark of ITW Chemtronics.

is dispensed through a felt tip. The ink can be drawn on to multiple substrates for the fabrication of conductive traces and jumpers. CircuitWorks conductive pen comes in two tip varieties, termed standard and micro-tip, allowing for two deposited line widths (actual line widths not reported) (*19*). The hand-held felt tip pen is able to deposit conductive elements on multiple materials and is not restricted to flat surfaces. However, these conductive pens have limited inks available, and do not allow for the use of laboratory developed inks.

3. Design and Proof-of-Concept

The PRINT system was conceived and developed in order to fill a technology need that existed in the direct write deposition facilities at ARL, and within commercially available direct write technologies. A customer research program required depositions of laboratory developed inks, with finished line widths of 220–350 µm on multiple substrates. It was determined that a technology did not exist that could provide for these feature sizes on substrates with complex topographies like textiles, textured surfaces, and woven fiber composites. It is possible that some of the techniques previously described could have been modified for surface mapping, and in-situ off-set adjustments; however, the research budget did not allow for such an investment. In answer, PRINT was developed; which is a contact-transfer direct write technique that provides for a constant feed, consistent deposition, and is viable for use on multiple materials and complex surface topographies. The deposition tip is a sphere or cylinder held in a socket or hub, which is coated in the desired ink by a feed chamber that is loaded by the storage cartridge. Spherical tips provide for easy deposition on to flat, uniform planes, and also for traversing of transitions on complex surfaces like textiles, fiber reinforced polymer composites, and other irregular surfaces. Cylindrical tips allow for wider lines and can be patterned in order to create a patterned deposition. The coated tip is then rolled across the substrate as the ink is transferred from the tip to the surface in order to obtain the desired deposition and eventual pattern needed. The deposited ink is then sintered, if required, with the aid of a trialing laser.

Figure 1 depicts two types of PRINT deposition tips. In both tips, section one is the storage cartridge for storing the inks that are to be deposited, which can be gravity or pressure fed. The cartridges are interchangeable, allowing for rapid material changes. Section two is the mounting junction and feed chamber, which loads the tip with ink. Section three is the deposition tip. There is a controlled gap between the feed chamber and the deposition tip that is manipulated depending on the viscosity, particle size, and particulate loading of the ink. Deposition thickness is dependent on the compatibility of the ink and surface, contact area of the deposition tip, and the properties of the ink.

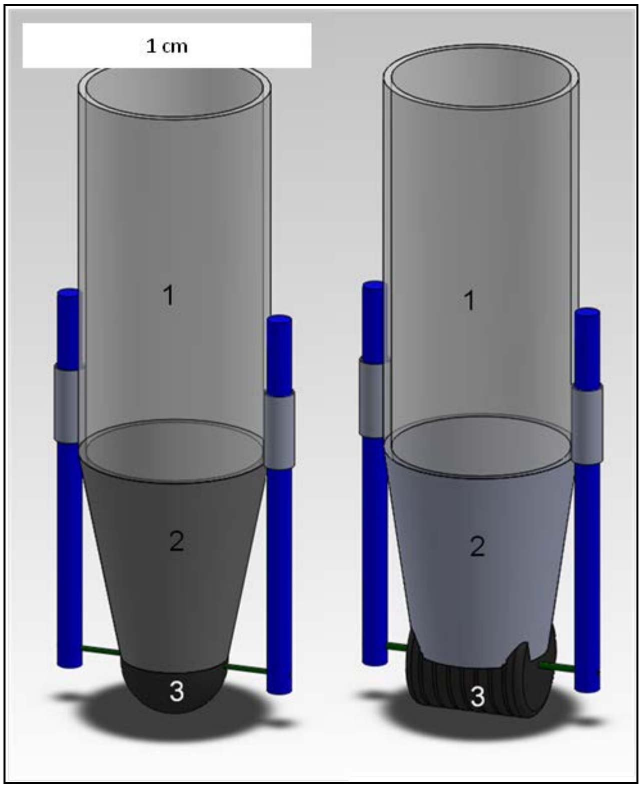

Figure 1. (Left) spherical deposition tip and (right) patterned cylindrical deposition tip.

Figure 2 is a representation of a spherical tip being trailed by a laser sintering mechanism. The laser can be used to sinter nano-particle inks, cure polymer inks, or aid in the evaporation of solvents. The laser can be disabled when not required.

After the initial design iterations, prototype deposition tips were developed. The spherical tip is a ball bearing with a machined central through hole. That hole houses an axel that is mounted to arms. The arms are mounted into sleeves on either side of the cartridge. Adjustments are made to the arms in the sleeves in order to accommodate different ink systems. Viscosity, particle loading, particle size, and wetability are used to determine the proper gap needed between the spherical tip and the feed chamber. Generally, higher the viscosity inks require a larger gap, and therefore the arms are extended to accommodate the increase in gap. A spherical deposition tip prototype, shown in figure 3, is applying a deposition of a laboratory formulated silver nano-particle ink. The PRINT deposition heads are very versatile and can be mounted on a Cartesian crosshead for deposition on two-dimensional surfaces, mounted on a multi-axis arm for deposition on three-dimensional surfaces, and even used in hand-held operation.

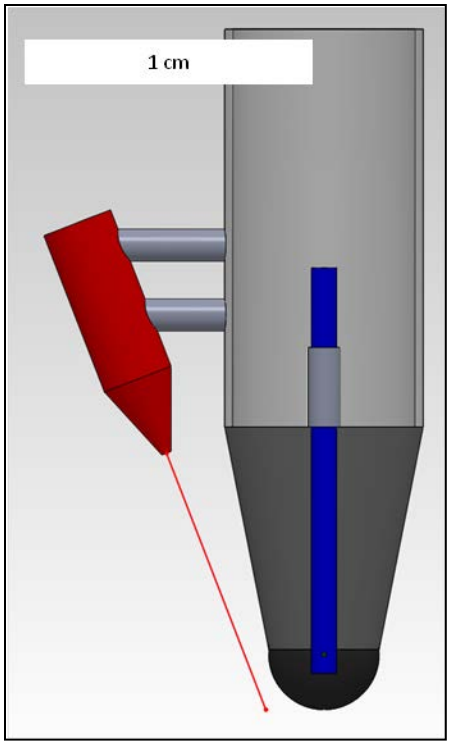

Figure 2. Spherical PRINT deposition head with trailing laser used for curing and/or sintering.

Figure 3. Spherical PRINT deposition head testing the deposition of silver nano-particle ink on a standard glass slide.

4. Evaluation

In order to test the capabilities of the PRINT technology, a commercially available direct write ink system was tested on multiple surfaces. The Cabot Conductive Ink CCI-300 (Cabot Corporation, Boston, MA) is a general use ink for the fabrication of conductive circuitry typically via high resolution inkjet printing (*20*). Hand drawn elements were deposited in order to verify that deposition could be obtained on multiple topographies. The depositions are depicted in figures 4–7.

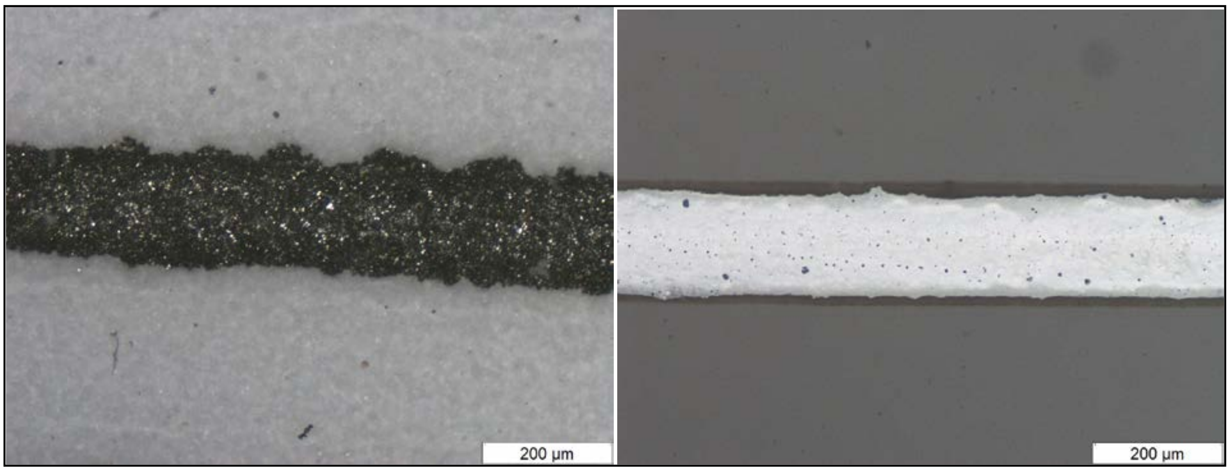

Figure 4. PRINT deposition of ink on (left) paper card stock, and (right) a standard glass slide.

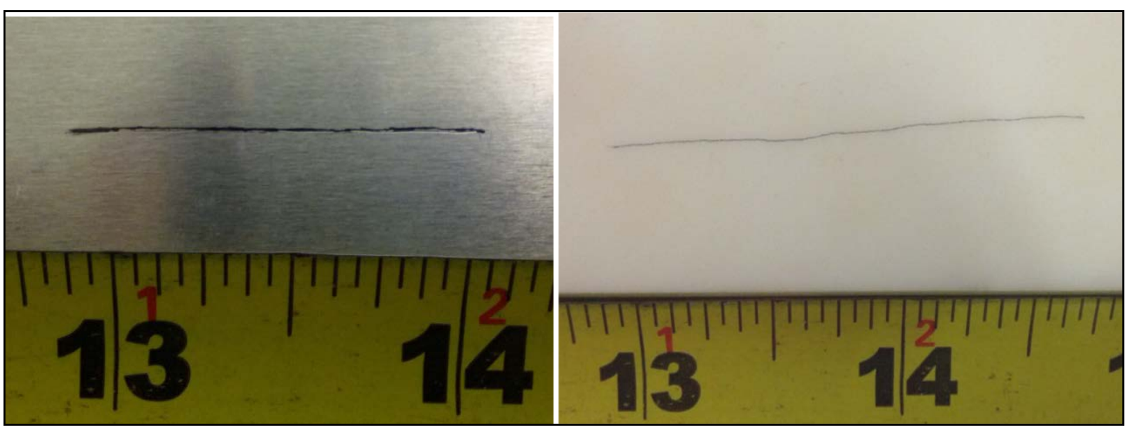

Figure 5. PRINT deposition on (left) polished aluminum sheet metal, and (right) aluminum oxide ceramic tile.

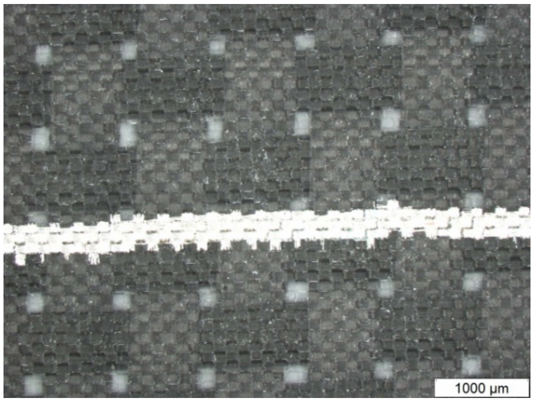

Figure 6. PRINT deposition on a plain weave carbon/epoxy composite.

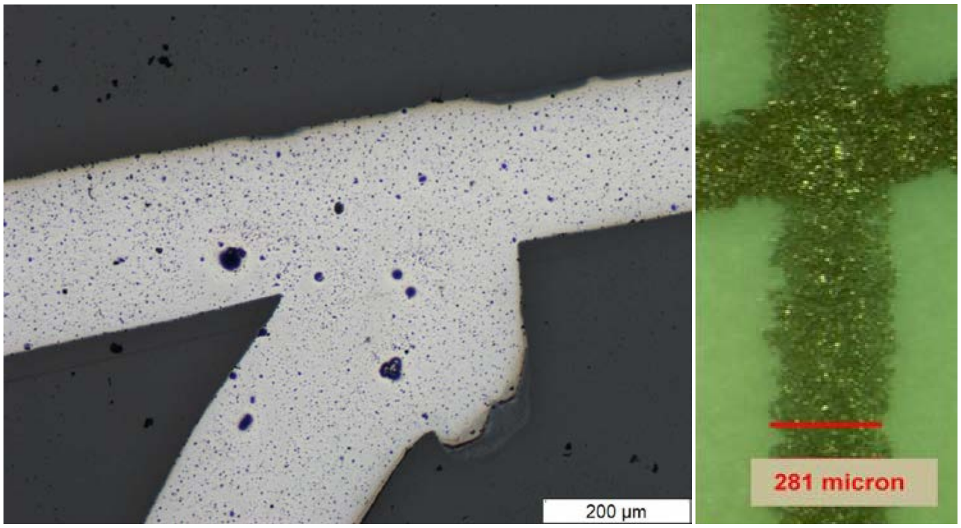

Figure 7. (Left) intersecting lines of CCI-300 ink deposited on a standard glass slide, and (right) overlapping lines on a painted metal surface.

The PRINT system was shown to be a viable technique for deposition of the CCI-300 ink system on the evaluated surfaces. In figure 6, the ink was deposited on the carbon fabric before curing, and wicked along the carbon fibers resulting in uneven edges. Absorption and spreading of the ink can also be seen as inconsistent edges on the paper substrate in figure 2. Direct writing of conductive and structural elements often involves the intersection and overlapping of line segments. In figure 7, an intersection of two line elements is shown on a standard glass slide with no visible separation at the junction. Figure 7 also shows that elements can be deposited in an overlapping manner, as depicted by the two line segments deposited on the painted metal surface.

5. Conclusions

A proof-of-concept direct write technique has been developed that allows for deposition on multiple substrates, and fills a previous ARL technology gap. The PRINT system can consist of a spherical or cylindrical deposition tip with interchangeable ink cartridges, and can be automated or hand operated. PRINT deposition tips are in direct contact with the substrate surface, and are able to follow contours of complex surface topographies. Because of this, there is no need for expensive three-dimensional surface mapping and computer controlled elevation changes, and automation would only require a low cost Cartesian system. The cylinder and spherical geometries of the PRINT deposition tips allow for surface contact at high angles of attack, and does not require the tip to remain perpendicular to the substrate.

Process optimization and automation of the PRINT system, along with characterization of deposited materials, processing characteristics, and material compatibility will follow in subsequent research documentation. It will also be determined if the definition of the tip is directly related to the line-width and edge quality of the deposition. This technology will be evaluated for the direct deposition of circuitry, including: sensors, connectors, switches, antennas, and other types. PRINT will also be evaluated for use in the fabrication of micro-composites by layered deposition.

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List of Symbols, Abbreviations, and Acronyms

AFM	atomic force microscope
ARL	U.S. Army Research Laboratory
DOD	drop-on-demand
DPN	Dip-pen nanolithography
FGDW	flow-guided direct write
LGDW	laser-guided direct write
LIFT	laser induced forward transfer
MAPLE DW	Matrix Assisted Pulsed Laser Evaporation Direct Write
PPL	polymer pen lithography
PRINT	Precision Rolled Ink-Nanoparticle Technology
tDPN	thermal dip pen nanolithography

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