Structure of Electrospray Printed Deposits for Short Spray Times

In electrospray printing, a plume of highly charged droplets is created from a conductive ink. Printing occurs by positioning a target substrate (TS) in the path of the emitted material. Here, the ink used is a colloidal dispersion consisting of nanoparticles suspended in a volatile solvent. The selection of a volatile solvent allows for rapid evaporation of the droplets in-flight to produce dry nanoparticles. A net electric charge is imparted on the emitted particles during electrospray. The interaction of this charge with the global electric field and with other charged particles/droplets governs the particles’ trajectory and determines the microstructure of the printed deposit. In this study, we characterized the structure of nanoparticle deposits printed using electrospray for deposits with low particle count. During printing, the TS was: (i) held stationary and (ii) translated with various short spray times and substrate velocities, respectively. Examination of both a static and translating TS provided fundamental insights into the printing process. Electrospray printing is capable of exerting much finer control over microstructure compared to other printing techniques. This has significant implications for the manufacturing of thin-films. [DOI: 10.1115/1.4037695]

1 Introduction

Electrospray is a technique that utilizes large electric potentials and hydrodynamic phenomenon to generate highly charged, monodispersed droplets from a liquid ink solution [1]. Under the influence of the applied electric potential, the ink solution at the emitter tip deforms into a Taylor Cone. At the apex of the cone, a jet is emitted and subsequently breaks up into droplets, which is responsible for the generation of the electrospray (Fig. 1). The emitted droplets are microns in diameter. Due to the high surface area to volume ratio of the droplets and the volatility of the solvent, the droplets experience rapid evaporation in-flight, resulting in dry deposition at the target substrate (TS) [2].

Electrospray has many promising applications due to a wide variety of available inks, including ceramics [3], polymers [4], and carbon nanotubes [5]. Viable candidate inks require high conductivity and low surface tension. In this study, we selected a model ink of polystyrene nanoparticles dispersed in methanol. During the electrospray process, nanoparticles are encapsulated inside the solvent droplets. These droplets undergo evaporation and Coulombic rupture in-flight until only dry nanoparticles remain. The now dry nanoparticles remain highly charged and are delivered to the ground plate by the applied electric potential. A wide variety of target substrates—including rigid glass, silicon wafers, or flexible polymers—can be positioned atop the ground plate. This target substrate will intercept the nanoparticles on their path to the ground plate and allow for material deposition. The electrospray printing process is performed under ambient conditions and does not require vacuum or extreme temperatures [6–8].

The substrate location and velocity can be controlled using linear stages or roll-to-roll systems.

The electric charge on the individual particles governs their deposition onto the target substrate. The “global” electric potential that is used to generate the electrospray is principally responsible

![Fig. 1 Electrospray printing of colloidal dispersions. The applied electric potential deforms the liquid meniscus at the end of the capillary tube into a Taylor Cone. A jet is emitted from the apex of the Taylor cone, which breaks up into highly charged droplets. In-flight, the droplets undergo rapid evaporation leaving dry material that is deposited on to the TS.](https://proceedings.asmedigitalcollection.asme.org/micronanomanufacturing/article-pdf/5/4/040906/5950370/jmnm_005_04_040906.pdf)
Electrospray printing has several unique advantages over other thin-film deposition methods [14,15]. Films manufactured using sputtering, evaporation, and chemical vapor deposition are inherently wasteful processes, as they require the removal of unwanted materials on the substrate using photolithographic patterning and wet/dry etching. Electrospray is an additive manufacturing processing technique (i.e., direct-write processing) which allows for targeted deposition only at desired locations. One of the advantages of electrospray compared to other direct-write processes is that it allows for fine control over deposition microstructure [16–18]. Specifically, electrospray allows for control over deposit characteristics such as layer thickness [8], nanoparticle spacing [19–21], and packing structure [22]. The ability to control deposit microstructure is of great importance because the structure of a printed deposit governs its functionalities.

Many applications would greatly benefit from the fine control over deposit microstructure offered by electrospray. For example, ordered, high-density deposits are used as antireflective coatings in solar cells [8,23] and for data storage [24]. Ordered, low-density particle films are used in biosensors [22] and for investigating nanoparticle materials [21].

Here, we investigate the structure of disperse (low-count) nanoparticle deposits (i.e., before the formation of multilayered structures) printed using (i) short spray times and (ii) fast substrate velocities. Due to the Coulombic interactions between particles (both in-flight and already deposited on the substrate), the evolution of a disperse nanoparticle deposit will significantly influence the final structure and functionalities of a deposit with higher particle counts. By investigating the structure of a disperse deposit, unique insights into the fundamental physics that govern the dynamics of the deposition process can be discovered.

2 Experimental Setup

One of the key advantages of electrospray is its modest instrumentation requirements (Fig. 2). Extreme environmental conditions such as high temperatures, pressures, or vacuum are not required. The electrospray originates from a glass capillary tube emitter. The glass emitter tips are pulled from an initial outer diameter and inner diameter of 1 mm and 0.58 mm, respectively, to a final desired diameter using a capillary puller (Sutter). For this study, the orifice sizes were limited to 60–70 μm, but larger or smaller emitter sizes are possible. For applications that require higher material throughput, an array of nozzles can be used in a multiplexed configuration. However, for this study, only a single nozzle configuration was considered. Tubing supplied fluid to the emitter tip via a manifold. A linear stage set the separation distance from the emitter tip to the target substrate at 7.5 mm. A syringe pump (Cole Parmer, Vernon Hills, IL) was used to provide fluid to the emitter at a flow rate of 0.2 μL/min. A high voltage (HV) supply (Spellman, Hauppauge, NY) provided high potential upstream of the emitter tip through a port in the manifold. Voltages of approximately 2 kV were required to establish a stable Taylor Cone and generate an electrospray. A 10 kV relay (Gigavac, Carpineteria, CA) activated and deactivated the high potential. The target substrate was placed on top of the ground plate. The ground plate was positioned atop a two-axis linear stage. These stages allowed for precise control of the target substrate’s position and velocity below the emitter. A machine vision system with a charge-coupled device (CCD) camera was used to monitor the formation and stability of the Taylor Cone during the printing process. The entire setup was controlled using LABVIEW (high voltage, linear stages, and machine vision system).

When first activated, the electrospray process can exhibit unpredictable emission. This start up effect can manifest as the emission of large droplets or instability in the Taylor Cone. Both of these will result in unpredictable and uncontrolled deposit morphology. To mitigate these very early time effects, a mechanical shutter was utilized to block deposition to the target substrate until a stable Taylor Cone was established. Using high-speed imaging (Vision Research, Wayne, NJ), the instability at startup was recorded to be approximately 10 ms. This established a lower bound on the time the shutter should remain closed, blocking the target substrate. In practice, the shutter was opened 5 s after the electrospray was activated.

High-resolution images of the printed nanoparticles were captured using fluorescent microscopy (Leica, Wetzlar, Germany) and an electron-multiplying CCD camera (Andor Belfast, UK). The raw images were captured with 14 bit resolution. Our model ink consisted of fluorescently labeled polystyrene particles dispersed in methanol at a volume fraction of 0.1% (v/v). Fluorescent particles

Fig. 2 Experimental Setup. A manifold is used to hold a glass capillary tube, which has been pulled to a fine tip. HV is applied to the fluid through the manifold. The nanoparticle ink is supplied to the emitter through the manifold using a syringe pump. A mechanical shutter is used to block material deposition on the TS until the spray is full developed. The separation distance between the emitter and the substrate is controlled in the x-direction using a linear stage. The substrate position is controlled in both the x- and y-direction. A machine vision system (M1) is used to observe the Taylor Cone formation and stability.

Fig. 3 Micrographs of typical electrospray printed deposits. (a) Stationary substrate with a spray time of 10 s and a separation distance of 7.5 mm and (b) Translating substrate with a velocity of 1 mm/s and separation distance of 7.5 mm. Both images were converted to binary and highly processed for visualization in this figure. The box along the center of the deposits represents the region of interest (ROI). In these regions, particle counts and locations are calculated for analysis. The height of the ROI is exaggerated for clarity. The scale bars are 750 μm.
3 Characterization of Deposit Structure

Nanoparticle deposits were printed onto 1 mm thick rigid glass substrates that were: (i) stationary and (ii) translating. For the stationary substrates, spray times from 3 s to 10 s were investigated. For the translating substrates, velocities from 1 mm/s to 10 mm/s were used. Shorter spray times and higher substrate velocities were not considered because the particle density was insufficient to allow for analysis.

Representative fluorescent images of the printed deposits can be seen in Fig. 3. The deposit in Fig. 3(a) was printed using a separation distance of 7.5 mm and a spray time of 10 s. The deposit in Fig. 3(b) was printed with a separation distance of 7.5 mm and a substrate velocity of 1 mm/s. The separation distance was found to govern the interparticle spacing but not the gross features of the deposit (for the stationary and translating substrate cases, respectively).

The deposit morphology was quantified by counting individual particles to plot a distribution. The deposits printed onto the stationary substrate were axisymmetric so it was sufficient to consider a ROI that bisected the deposit. For particles printed onto the translating substrates, the length of the printed line was sufficiently long to create a region that was fully developed and free of edge effects associated with starting and finishing the translation of the stage. For these deposits, the ROI was selected in the fully developed region and was perpendicular to the direction of substrate travel. To create the ROI, overlapping, high-magnification images were taken along the deposit as shown in Fig. 3. Adjacent images were offset by approximately 50% and were taken continuously across the deposit. The height of the ROI was governed by the frame size of the electron-multiplying CCD camera, and the width was governed by the width of the printed deposit. Once the images over the entire ROI had been taken, they were stitched together using ImageJ to form a single image spanning the entire deposit.

The single stitched composite image was transferred to MATLAB to analyze the deposit structure. After filtering, the centroids of each particle were located using a two-stage particle-tracking algorithm. The first stage computes the center of each particle using the local intensity maxima. This initial centroid calculation had pixel level accuracy. The second stage of the algorithm then computes a weight average around each local maxima to find the centroid of each particle with subpixel accuracy. After the location of the centroids have been computed, the particle distribution across the deposit was obtained. The deposit was first divided widthwise into bins. The width of a bin was selected such that it spans 1% or 2% of the width of the deposit for the stationary or translating substrates, respectively. The difference in bin widths was due to a relatively smaller deposit width for the translating substrate. This nondimensionalization was selected to allow for deposits of different widths to be directly compared.

3.1 Stationary Substrate. Deposits printed at the three spray times investigated (3 s, 6 s, and 10 s) all exhibited similar gross structure to that seen in Fig. 3(a), but with different particle counts. For all spray times, the printed deposits exhibited the same characteristic bimodal particle distribution with a pronounced outer edge, an enhanced center region and a depletion region with a lower particle count in between (Fig. 4(a)). The top left panel of Fig. 4(b) shows the average particle count as a function of spray time. The other panels are high magnification images taken at the outer ring of the deposit (i.e., the region of highest particle density). As expected, from Fig. 4(b), it can be seen that the particle number increased with spray time. However, the size of the printed deposit remains constant on the time scales examined in the study. Increasing spray time only serves to increase the particle count within the printed deposit.

3.2 Translating Substrate. Deposits printed at the three different substrate velocities (1 mm/s, 5 mm/s, and 10 mm/s) all exhibited the same gross structure as seen in Fig. 3(b), but with different particle counts (Fig. 5(a)). For each velocity, the printed deposits showed uniform particle coverage across the printed line. The top left panel of Fig. 5(b) shows the average particle count as a function of substrate velocity. The other panels are high magnification images taken at the center of the printed line. The particle count was inversely proportional to the substrate velocity. However, the width of the printed lines remains constant for all substrate velocities considered in this study. Increasing the substrate velocity only served to decrease the particle count within the printed deposit.

![Fig. 4](https://proceedings.asmedigitalcollection.asme.org/doi/10.1115/JMNM.2017.040906.3)

(a) Particle count for typical electrospray printed deposits on a stationary substrate. The horizontal axis has been normalized to go from edge to edge of the deposit. The vertical axis represents particle counts across the ROI. Above the plot are the composite images of the ROI for each distribution, with spray time increasing from the top to the bottom image. The contrast of the images has been greatly increased for visualization. (b) With increasing spray time, the particle density of the printed deposit increases. The upper left panel is the average particle count for three spray times (3 s, 6 s, and 10 s) across the entire ROI. Each spray time is the average of at least three deposits. The error bars are one standard deviation. The other panels are images taken at the outer ring (i.e., the area of highest particle density) for each spray time. The inset scale bars are 10 μm.
4 Discussion

In order for electrospray to become a viable technique for manufacturing, it is critical to characterize the influence of each of the processing parameters on the final structure of the printed deposit. The applied electric potential, required to generate the electrospray, imparts a net electric charge onto the printed nanoparticles. This net charge governs the deposition of the individual nanoparticles. Their delivery from the emitter to the target substrate is primarily determined by the global electric field. The radial distribution is governed by the mutual Coulombic interactions between the particles and solvent droplets in-flight. As seen in Figs. 4 and 5, the lack of an evaporatively driven morphology (i.e., “coffee-ring” deposition) means the solvent completely evaporated in-flight, leaving only dry nanoparticles. This allowed the electric charge to dominate, creating a deposit with isolated particles on the substrate. The deposited nanoparticles remain isolated from each other for some period as they maintain their electric charge. It is possible to obtain a tightly packed particle structure by printing for sufficiently long times. This time scale has been found to be dependent on the electric properties of the target substrate. The mechanism of the charge decay is unclear and will be the focus of future studies.

The deposits printed onto the stationary substrate exhibit a bimodal distribution for all spray times. It is speculated that the bimodal distribution is due to the segregation of nanoparticles that occur in-flight because of the mutual Coulombic interactions within the plume. Most of these interactions are likely to occur near the emitter, prior to complete evaporation of the solvent, where the droplet density is highest. As seen in Fig. 6, particles that are initially near the central axis have approximately an equal distribution of charged particles/droplets in each direction. This distribution will result in a low net radial force on the nanoparticles, which will remain along the midline of the plume during transport from the emitter to the target substrate. Particles that are initially located off the central axis of the plume are surrounded by an unequal charge distribution with a higher concentration near the central axis. This asymmetric charge distribution will result in a net radial force on these nanoparticles (i.e., while they are in-flight) that is directed outward toward the edge of the plume. These particles will be transported to the edge of the plume and are responsible for the edge enhancement seen on the target substrate.

For printing on to the stationary substrate, there is an area of high particle count at the center of the deposit. Moving radially outward, there is a depletion region of low particle count resulting from the segregation in-flight. At the edge of the deposit, a thickening occurs to form an outer ring along the perimeter. For sufficiently long spray times, it is possible to obtain deposits in which there is direct particle-particle contact. For printing onto a rigid glass substrate, deposits must be sprayed for tens of minutes to allow the charge on the deposited nanoparticles to dissipate, permitting subsequent particles to land in contact. The electric

![Fig. 5](https://proceedings.asmedigitalcollection.asme.org/proceedings/pdf/5/4/040906-4/040906-4.pdf)  
Fig. 5 (a) Particle count for typical electrospray printed deposits on to a moving substrate. The horizontal axis has been normalized from edge to edge of the printed line. The vertical axis represents particle counts across the ROI. (b) With increasing substrate velocity, the particle count in the ROI decreases. The upper left panel is the average particle count for three different substrate velocities (1 mm/s, 5 mm/s, and 10 mm/s) across the entire ROI with error bars of one standard deviation. The other panels are images taken at the center of the printed line (i.e., area of highest particle density) for each substrate velocity. The inset scale bars are 10 μm.

![Fig. 6](https://proceedings.asmedigitalcollection.asme.org/proceedings/pdf/5/4/040906-4/040906-4.pdf)  
Fig. 6 Particles in-flight experience a mutual force from other droplets/particles that are also in-flight. This mutual force is responsible for the radial distribution of particles on the substrate. (a) Particles near the center of the plume have a negligible net mutual force and (b) particles further away from the central axis of the plume experience a net force outward. This is responsible for the high particle density at the center and edge of the deposit.

![Fig. 7](https://proceedings.asmedigitalcollection.asme.org/proceedings/pdf/5/4/040906-4/040906-4.pdf)  
Fig. 7 Simulated particle count plot for a moving substrate based on the profile of the 3 s stationary printed deposit. (a) A stationary profile is generated by rotating the 3 s radial profile 2π around the central axis and (b) the stationary profile was translated to replicate the substrate velocity. The edge and center regions of the deposit still exhibit high particle counts (this is not seen in experiments). The depletion region has a relatively higher particle count than the static profile. This is potentially due to the blurring from the edge-enhanced region.
properties of the target substrate can potentially be tuned to alter the time scale of the charge dissipation on the deposited nanoparticles.

The introduction of relative motion between the target substrate and the emitter increased the uniformity of the printed deposits compared to the static configuration for all translation velocities. This result is consistent with previously reported research with nonvolatile, pure liquid sprays [25–27]. This previous work accounts for the increased deposit uniformity by considering the material flux at the target substrate. In particular, the higher droplet count that is observed at the edge of the plume is balanced against the smaller droplet size of this thickened region. Meanwhile, droplets at the center of the plume are larger and less numerous. It is this relative balance of material flux that is believed to be responsible for the observed uniformity.

However, the material flux explanation does not fully capture the mechanisms governing the deposition of nanoparticles reported here (i.e., from a colloidal ink). This is highlighted by using MATLAB to translate a stationary deposit profile along a line (Fig. 7). This was accomplished by reconstructing the (axisymmetric) stationary profile for a 3 s spraying using the particle distribution from the ROI. The radial profile was first rotated a complete revolution around the central axis to create a stationary, circular distribution (Fig. 7(a)). The stationary profile was continuously shifted by one bin in the print direction. After each step, the running total of particles in each bin along the transit direction was updated. The translated profile still exhibits the characteristic center and edge enhancement observed for the stationary profile (Fig. 7(b)). Note that the features are less clear with the introduction of substrate velocity due to blurring from the edge-enhanced region. We contend that an additional mechanism must contribute to the final deposit morphology of the printed line that is not captured by a simple translation of the stationary deposit profile. One possibility is the disruption of the axisymmetry of the printing configuration. The introduction of substrate motion increases the space charge “behind” the emitter. This addition of charge may influence subsequent particle deposition to promote an increase in film uniformity. Another potential mechanism to explain the uniformity observed in the printed lines is the translation of the dielectric target substrate. Dielectric substrates experience an induced surface charge when exposed to the global electric field required to establish the electrospray. The induced surface charge is a function of the substrate location relative to the emitter tip (i.e., the location with the largest magnitude of induced charge is directly below the emitter tip). The introduction of substrate motion creates a migration of charge (induced current) along the surface of the target substrate. This induced current could influence the particles in-flight and ultimately lead to an increase in uniformity of the deposited nanoparticles. While it is worthwhile to note that the simulation results for pure solvent spray and the previously reported research with pure solvent sprays [26–27]. This previous work accounts for the increased deposit uniformity by considering the material flux at the target substrate. In particular, the higher droplet count that is observed at the edge of the plume is balanced against the smaller droplet size of this thickened region. Meanwhile, droplets at the center of the plume are larger and less numerous. It is this relative balance of material flux that is believed to be responsible for the observed uniformity.

5 Conclusion

The structure of disperse (low-count) electrospray printed deposits provides critical insights into the physics that govern the printing process. The trajectory of the emitted particles is determined by the primary electric field and the Coulombic interactions among neighboring particles/droplets. Both the static and translating printing configurations produce consistent gross deposit structures for a range of spray times and substrate velocities, respectively, with only changes in the interparticle spacing. Understanding the relationship between processing parameters and deposit structure is necessary if electrospray printing is to be used in the manufacturing of thin-films. Future work should investigate the mechanisms that lead to increased deposit uniformity for the case of substrate translation and an examination of morphology transitions for higher particle count deposits.

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References


