Morphology of printed lines and droplet deposits using hydrophilic nanoparticle suspensions

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This paper focuses on the morphology of continuous mode printed lines of a generic polymer suspension. The suspension consists of carboxylate nanoparticles. The printing is performed by forming a stable capillary-bridge of the suspension between the print-nozzle and glass substrate. The printed deposits are examined microscopically. The printing technique used here is easy to implement and allows a wider property window for the fluids that can be printed compared to drop on demand mode printing. The morphology of these printed lines is found to be dependent on the number of layers of the nanoparticles present. To further understand the fundamental mechanism of printed nanoparticle deposit morphology development, droplet deposits of the suspension are also prepared and analyzed.

Background

Fabricating increasingly smaller electrical components has been an area of interest for the last 20 years. The current industrial fabrication techniques for such electrical circuitry are primarily lithography based. The lithographic techniques are well suited to miniature circuit fabrication. However, these techniques can be inefficient for large area electronics applications such as large flexible displays on polymer substrates, RFID tags, etc and hybrid electronics applications. Environmental impacts of relatively large chemical wastes produced in fabrication of such large area circuits via lithography is another important concern.

Printing of nanoparticle suspensions of functional materials directly on a substrate offers a means to overcome these problems of lithographic techniques. The printable suspensions contain nanoparticles of a metal or a polymer that have desired electrical properties. The suspension is printed onto the substrate forming a desired two or three-dimensional pattern.

Essentially, printed line patterns are the basic unit of printed fabrication. The printed lines can be the final element of fabrication, for example when making interconnects for two circuit elements, or they can be building blocks for a particular circuit element. In general, the interconnects prepared by printing techniques, can be \( \sim 100 \mu m \) wide, however, a recent technique reports successful reduction of printed feature sizes down to 1 \( \mu m \). Therefore, printing lines containing nanoparticles has emerged as an efficient way to create printed electronics circuits without costly and time consuming lithographic techniques. The two most common techniques of printing electronic circuits are drop on demand (DOD) mode printing, and continuous mode line printing. DOD technology involves creation of individual droplets of 10-70 \( \mu m \) diameter that are ejected through a nozzle. These droplets are spaced so that the individual droplets overlap one another forming a solid line. The second method of fabricating an electrical interconnect between electronic components is by continuous mode line printing. The continuous mode printing traditionally involves development and controlled break up of a suspension jet by Rayleigh instability. The techniques used in this work is different in that we make a continuous capillary-bridge of liquid between the substrate and needle tip through which the suspension flows, leaving a line that contains the nanoparticle suspension.

The morphology of printed lines has important implications to the application of the printing techniques. For example, deposits of hydrophilic nanoparticles on hydrophilic substrates can lead to crack formation, which can affect the electrical properties of the deposit (see Figure 1). The primary goal of this work is to investigate the morphology of printed deposits and develop strategies to manipulate the morphology to serve specific application requirements.

It is hypothesized that the average number of layers of the nanoparticles, which corresponds to the thickness of the printed line, is the reason for the presence or absence of cracks in printed line deposits. The stability of a deposit is dependent on the number of nanoparticle layers. An increase in the number of layers results in a more unstable deposit and lines with larger crack feature size appear when compared to lines with fewer layers, which are more stable. Also investigated was the importance of a “coffee stain” effect in these printed lines. The “coffee stain” effect would lead to a gathering of the nanoparticles at the edges of the printed lines where the cracking would develop due to a higher number of nanoparticle layers being present leading to decreased stability. In addition, to clarify the effect of geometry, if any, on the morphology of printed deposits, the suspensions are also used to prepare droplet deposits. The development of cracks in this hemispherical geometry is analyzed and compared with the morphology of printed lines.

Lines were also printed of a nanoparticle copper suspension to make morphological comparisons to lines printed with a hydrophilic nanoparticle (carboxylate)
FIG. 1: Photograph of a line printed with commercial carboxylate nanoparticle suspension, that demonstrates a characteristic cracked morphology throughout the ∼2 mm printed line.

FIG. 2: Schematic of the capillary-bridge based continuous mode printing setup. The droplet formed at the needle tip creates a capillary-bridge between the needle and moving substrate.

Materials and Experimental

Polybead carboxylate nanoparticle suspensions are chosen as a generic hydrophilic polymer nanoparticle suspension. The suspension consisted of spherical nanoparticles with a nominal particle diameter of 0.0458 µ and a concentration of 2.65% by weight. According to the manufacturers specifications, the suspensions are stabilized using a proprietary surfactant formulation. The solvent used is water.

The needle tips used here were 30 gauge needles from EFD, Inc. (with inner diameter of 150 µm and outer diameter of 250 µm).

The lines were printed on cleaned glass slides. The slides were cleaned by repetitive washing in ethanol and de-ionized water. The capillary-bridge based printing setup consisted of a syringe pump, a visualizing screen, and a computer controlled motorized platform for the substrate motion. The syringe pump was used to control the suspension flow rate, which was varied from 0.1 to 1 ml hr⁻¹.

To print lines on the glass substrate, the substrate is placed on the moveable platform and the needle tip height is adjusted so that the substrate will come in contact with the droplet forming at the tip of the needle. This resulted in formation of a capillary-bridge of suspension between the needle tip and the substrate (see Figure 2). A miniature camera connected to the apparatus allowed easy adjustment of the needle distance above the substrate and helped in forming a stable capillary-bridge.

The suspension is continuously pushed through the needle and the substrate underneath is moved with computer-controlled movement of the platform. This leads to the formation of a continuous printed line of the suspension. The substrate is leveled with two leveling screws on the moving platform to ensure that the capillary-bridge is not disrupted during the substrate motion. The substrate velocity was capable of being varied in the range of 5 mm s⁻¹ to 12.5 mm s⁻¹.

In order to create droplet deposits, a small amount of suspension was pushed through the needle tip and the droplet was allowed to contact the substrate. Droplet deposits with diameter value ranging from ∼2,000 µ to 100 µ were prepared by this technique.

In order to determine the effect of evaporation on the formation of deposits, droplets were allowed to evaporate through several methods, each method was designed to alter the evaporation rate across the droplet. The simplest method for droplet evaporation was to expose the droplet to ambient air in the lab. In order to control the droplet evaporation two other arrangements were used. In one arrangement, droplets were created beneath a 2 mm metal cap with an opening of 0.5 mm cut in its top. In another arrangement, the same cap was placed on top of a droplet that had already begun evaporating in the ambient air. A schematic of the cap is shown in Figure 3.

Droplets were placed beneath the cap using the syringe pump-camera system described above. The method for placing a droplet beneath the cap was to lower the needle through the opening of the cap and then place a droplet onto the glass substrate through the opening in the cap (see Figure 3). Setting the syringe pump to a flow rate of 0.1 ml hr⁻¹, the needle was lowered to contact the substrate after ∼7 seconds. This resulted in a droplet deposit with a diameter ∼1 mm. Sending the needle through the open-
Schematic of cap used to test the influence of evaporation rate on the morphology of droplet deposits. This metal cap was used to cover drying suspension.

Suspensions of copper nanoparticles were created in lab. The partially passivated copper nanoparticles, with nominal diameter of 25 nm, were suspended in a solution of Poly(ethylene oxide) (PEO) in a mixture solvent of toluene/terpineol in 20:80 ratio by weight. The concentration of PEO was 0.5% by weight. The solution was prepared by continuous gentle stirring on a hot plate set at 65°C. When the PEO was completely dissolved copper nanoparticles were added so that the final suspension was comprised of 15% copper nanoparticle by weight.

Results and Discussion

Lines

Generic hydrophilic nanoparticle suspensions were printed as lines using the capillary-bridge based printing technique. The printed lines displayed several different morphologies. Simple volumetric calculations were performed to determine the average number of nanoparticle layers present in the printed lines.

\[ H = \frac{Q \cdot C}{W \cdot u} \]  

For equation 1 \( H \) is the height of the line, \( Q \) is the volumetric flow rate, which varies, \( C \) is the concentration of nanoparticles, 2.65%, \( W \) is the width of the printed line, which varies, and \( u \) is the velocity of the substrate, 5 mm/s. It was observed that at higher speeds, up to 12.5 mm/s, the width of the printed line decreases, however the line formed at higher speeds suffered from discontinuities. Due to the discontinuity issues experiments shown here were done with a substrate velocity of 5 mm/s. For equation 2 \( LP \) is the estimated number of layers and \( D \) the nominal diameter of the nanoparticles, 0.0458 µm.

Figure 4 compares the effect of suspension flow rate on the morphology of the printed line from carboxylate suspension. Table I summarizes the lines printed and their measured and calculated dimensional properties. For 0.1 ml/hr flow rate (Figure 4(a)), the resulting line-width was \( \sim 1 \) mm with \( \sim 3 \) nanoparticle layers, where the latter was estimated using Equations 1 and 2. Because of the low number of layers the deposit is stable and visible cracks are unable to form. On the other hand, for 0.3 ml/hr flow rate, the resulting line-width was \( \sim 1.2 \) mm with \( \sim 8 \) nanoparticle layers, as shown in Figure 4(b). It is observed that at this flow rate, crack development is sensitive to the width of the line. A change in the line width

\[ LP = \frac{H}{D} \]
TABLE I:

<table>
<thead>
<tr>
<th>Description</th>
<th>Line A</th>
<th>Line B</th>
<th>Line C</th>
<th>Line D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate ($\frac{ml}{hr}$)</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Width of Line (cm)</td>
<td>0.1107</td>
<td>0.1253</td>
<td>0.1624</td>
<td>0.1923</td>
</tr>
<tr>
<td>Height of line (mm)</td>
<td>0.13</td>
<td>0.35</td>
<td>0.45</td>
<td>0.76</td>
</tr>
<tr>
<td>Diameter of Particle (mm)</td>
<td>0.0458</td>
<td>0.0458</td>
<td>0.0458</td>
<td>0.0458</td>
</tr>
<tr>
<td>Average Layers of Particles</td>
<td>2.8</td>
<td>7.6</td>
<td>9.8</td>
<td>16.6</td>
</tr>
</tbody>
</table>

The physical mechanisms that are responsible for this change in morphology are present in Figures 4(c) and 4(d) which were printed at flow rates of 0.5 and 1 $\frac{ml}{hr}$, respectively. These effects are even more prominent in Figure 5 and are discussed in the following.

In Figure 5(a), the printed line shows clear cracks at the edges and no visible cracking at the center. The cracking along the edges is due to a “coffee stain” effect, which causes a higher accumulation of nanoparticles to be present at the edge, and therefore greater number of nanoparticle layers. This movement of nanoparticles towards the edges would also result in a decrease in the number of layers at the center of the line, which can result in elimination of visible cracks formation in the center.

Figure 5(b) shows a printed line with a width $\sim$1.5 mm, where the cracks form only at the center of the line. This can be understood as follows. It has been observed that for these types of lines, the contact line does not remain pinned for more than a few seconds, instead the contact line recedes towards the center of the line. Contact line pinning is a critical part of the “coffee stain” effect. The lack of contact line pinning is responsible for the resulting deposits to be more uniform from the center to the edges of the lines. As an extension, a rapidly receding contact line allows the particles to concentrate at the center of the deposit, which would create more nanoparticle layers and can lead to cracking at the line center (seen in Figure 5(b)).

Deegan et al. found that a “coffee stain” effect will create a higher concentration of solute at the edge of a droplet deposit if three conditions are met: the droplet has a nonzero contact angle, the contact line remains pinned and the solvent evaporates. In our experiments with printed lines, the contact angle is nonzero and the solvent fully evaporates. The pinned contact line is important part of the ensuing fluid flow that sends the solute towards the edges. Droplets and printed lines have a higher evaporation rate at the edges due to a higher radius of curvature at the edges. If the contact line is pinned, a replenishing flow of fluid must travel to the edges to compensate for the higher evaporation rate. If the contact line was not pinned, there would be no need for a replenishing flow and the contact line would recede with more material being present in the center of the deposit. These physical mechanisms play an important part in determining the number of layers present across the width of the line.

It is important to note that there was no difference in the process used to create the two lines shown in Figure 5. For a given flow rate, the printing set up could produce lines with their widths reproducible within $\sim$200 $\mu$m of one another.

From the images in Figures 4 and 5 and the information presented in Table I, it can be inferred that the number of nanoparticle layers needed for crack formation is between 8 - 17 layers. However, it is important to understand...
stand that due to the number of layers being nonuniform along the width of the line, the average number of layers does not represent a uniform distribution across the line. Nonetheless, it is certain that there must be at least 8 layers for visible cracks. For the upper limit of 17 layers of nanoparticles, as in Figure 4(d), visible cracks develop throughout the line.

The lines containing between 8-17 particles layers and those containing above 17 layers appear to have a morphology that combines the pinned contact line with the receding contact line effects. In this combined effect, there is enough contact line pinning initially for nanoparticles to be present at the edges of the line. However, after a period of time, the contact line becomes unpinned and begins to recede. When the contact line begins to recede there is still enough nanoparticles present in the liquid to allow for nanoparticles to form thick enough deposit away from the edges the line. This is clear from the cracks developed printed lines shown in Figures 4(c) and 4(d).

Lines printed at 0.5 ml/hr flow rates, result in line-widths of \( \sim 1.2 \text{ mm} \), and have \( \sim 10 \) nanoparticle layers. These lines exhibit the cracking both along the center and at the edges. However, in between the center and the edges there is a space where no visible cracks develop. The flows present due to the contact line pinning initially resulting in a “coffee stain” effect and the gathering of material at the center of the line due to a receding contact line leave parts in between where there number of nanoparticle layers are not enough to allow cracking. The average number of nanoparticle layers (10) is close to lower limit of the estimated minimum number of layers necessary for crack formation (8). Therefore, a fluid flow pattern that leads to more particle layers in some preferred parts across the line width can result in other parts being unable to form visible cracks. This is what is observed in lines printed at this flow rate (Figure 4(c)).

Lines printed at 1.0 ml/hr result in line-widths \( \sim 2 \text{ mm} \), and with \( \sim 17 \) nanoparticle layers, more than any other flow rates considered in this work. Because of the comparatively high number of layers, cracks develop throughout the entire width of the line (Figure 4(d)). The “coffee stain” and the receding contact line effects, which create more layers at the edges and center of the printed line, are still present as manifested by more prominent cracks in these parts.

### Droplets

The droplets were seen to develop several different repeatable morphologies based upon how they were allowed to evaporate as shown in Figure 6.

Because of difficulty in accurately determining the volume of a droplet suspension that is placed on a glass substrate by directly contacting the substrate with a needle tip, no estimates were reliable enough to determine the estimated average number of nanoparticle layers in the resulting deposits. Droplets that were allowed to evaporate in ambient air, and that had a diameter larger than \( \sim 1 \text{ mm} \), were seen to develop cracking through the entire deposit (Figure 6(a)). The cracking in this deposit also was more prominent at the edges than in the center, and the cracks developed in a radial pattern that moved from the edge towards the center of the droplet. The second kind of morphology was obtained from droplets that had a cap placed over them (Figure 6(b)) so that the

![FIG. 6: Three droplets of carboxylate nanoparticle suspension with diameters \( \sim 1 \text{ mm} \). Droplet (a) was allowed to evaporate in ambient surroundings. Cracks are formed through out the droplet deposit. Droplet (b) was made to evaporate beneath a cap placed on top of the droplet, the droplet was not placed directly beneath opening in cap. Here the cracks develop only along the edges of the droplet. Droplet (c) was formed by creating a droplet beneath the cap to ensure that the droplet was placed directly beneath the opening in the cap. Here cracks have developed only at the center of the deposit, near the nanoparticle agglomerates.](image-url)
opening in the cap was not directly above the droplet. The cracks that developed at the edges of these droplets had a wave pattern that travels around the circumference of the droplet. The last type of morphology were formed from droplets that were deposited by inserting a needle tip through the opening and placing a droplet directly beneath the opening. This creates droplets that exhibit almost no cracking around the edges and particle agglomerates are spread throughout the deposit. Evaporating droplets directly beneath an opening in a cap has been shown to reverse the “coffee stain” effect. Droplets that are formed in this manner exhibit almost no cracking along the edges and only slight cracking around the nanoparticle agglomerates. It is found that by placing a cap on top of an existing droplet it is possible to influence the formation of cracks in a droplet deposit. Also, creating a droplet beneath a cap leads to an aggregation of particles primarily at the center of the droplet on the substrate.

Crack Orientation

In applications involving printed lines that display these types of cracks it is important to understand how the cracks are orientated. It has been observed that the orientation of the cracks will follow the contact line seen in Figure 7.

When droplets are allowed to evaporate in ambient conditions the contact line moves from the edge of the droplet towards the center, while maintaining its circular shape. This results in radial crack development, with the cracks approximately perpendicular to the contact line. However, when droplets are placed under a cap the way the contact line moves would not follow this pattern; although the exact motion of the contact line in this case remains unknown as our set up did not allow its visualization.

Therefore, controlling the way a line or droplet evaporates along with control of the approximate layers of nanoparticles appear to be two methods for printing a suspension line or droplet with a desired deposit morphology.

Printing Metal Nanoparticles

In order to directly approach the printing of potentially viable interconnects, lines were also printed using an in-house created copper suspension. A line of printed copper suspension can be seen in Figure 8.

The lines created from this suspension do not display cracking throughout the line. Instead the printed lines display agglomerates inside the line with no noticeable order. The deposits in both the commercial carboxylate suspension and copper nanoparticle suspension have similar geometry. Therefore, the evaporation flux in the printed patterns is expected to have similar profile for either suspension. The significant difference in the morphology of the lines printed from these two suspensions indicates that rheological properties of the suspension being printed have strong influence on the morphology of the printed line deposits. In the case of copper nanoparticles suspended in viscoelastic PEO solution, the viscoelastic forces can negate the “coffee stain” and receding contact line effects that were found responsible for the cracked morphology of the carboxylate particle suspensions.

Conclusion

In order to make printed electronic circuits with well-controlled electrical properties, it is necessary to control the morphology of the printed lines containing nanoparti-
FIG. 8: Image taken of a continuous mode printed line of 15% copper by weight suspended in a PEO solution. This image does not display cracks.

cles. We have shown that cracking can take place in these printed lines. A range of the number of particle layers (8-17) was found to be necessary for development of such cracks. Formation of such cracks is explained in the context of capillary instability, coffee-stain effect and the receding motion of suspension contact line on the substrate. These effects cause more nanoparticles to be present at the edges and the center of the lines and thus local formation of cracks develop in these parts. The strategies based on controlling the evaporation flux of drying suspension deposit are proposed as ways to control crack formation in the deposits. Experiments performed with a suspension of copper nanoparticles show that crack development is dependent on the rheological properties of the suspension printed. The viscoelastic forces in the copper nanoparticle suspension were strong enough to avoid formation of any cracks in the corresponding printed line deposits. The fundamental knowledge obtained here will be useful for development of printed electronic applications.

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