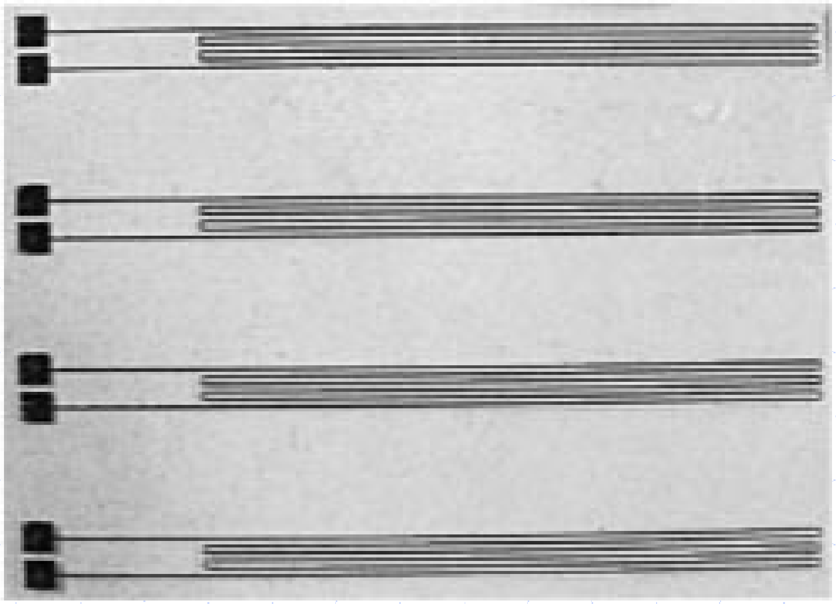
Morphology of printed lines and droplet deposits using hydrophilic nanoparticle suspensions

By Jim Lyon

REU Advisor Professor Megaridis

Background

- Printed lines containing micro-particles are used in development of printed wiring boards (PWB)
- The morphology of the printed lines would have an effect on the bulk electrical properties of the printed line
- These lines containing nanoparticle suspensions can be fabricated at a lower cost than commonly used lithographic techniques



Example of complex conductive patterns printed using a gold nanoparticle suspension the line widths are on the order of 100 microns[1]

1) Szczech, J.B., et al, *Electronics Packaging Manufacturing, IEEE Transactions on* , vol.25, no.1, pp.26-33, Jan 2002

Goals

- Learn how to use the experimental setup
- Print model nanoparticle suspensions and investigate the morphology of printed lines and droplets
- Determine the effect of geometry on the morphology of deposits

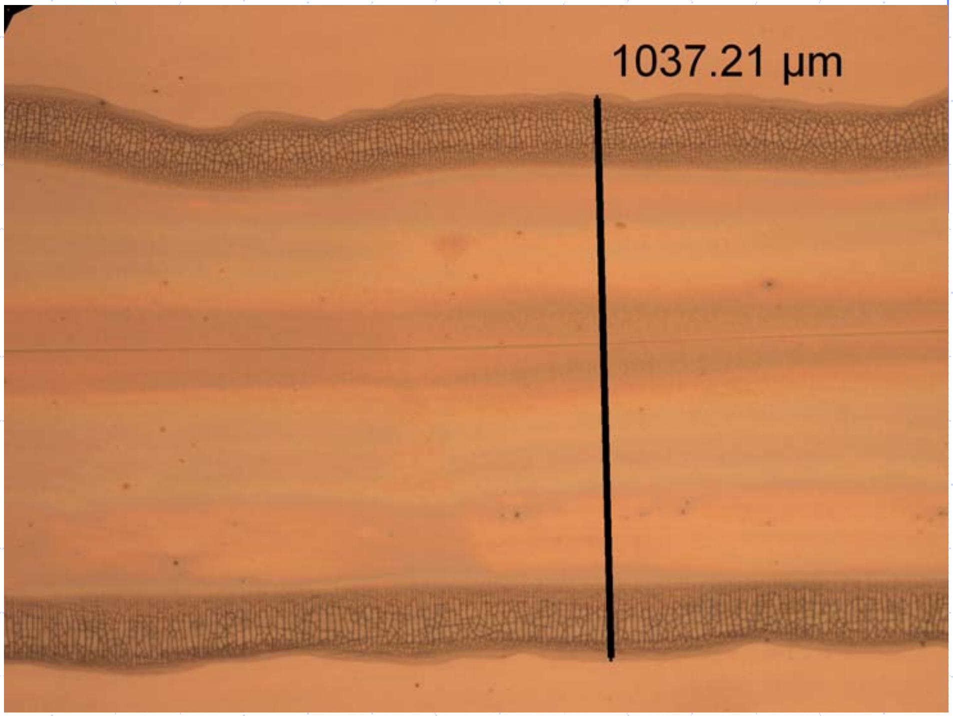


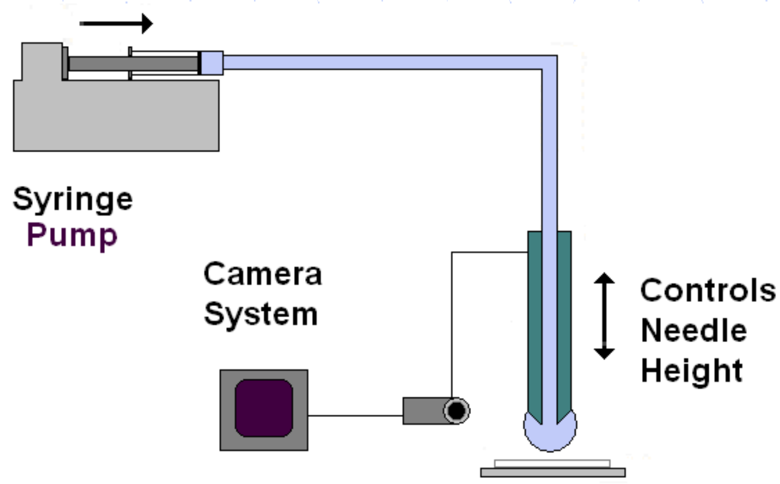
Image of a printed line of a hydrophilic nanoparticle suspension

Generic Polymer

- Polybead® Carboxylate nanoparticle suspensions are chosen as generic hydrophilic polymer nanoparticle suspensions
- The suspension consisted of spherical nanoparticles with a nominal particle diameter of 0.0458 μ
- Concentration of the polymer was 2.65% by weight with the remaining suspension being composed of an unknown combination of water and surfactant

Droplet Experimental Setup

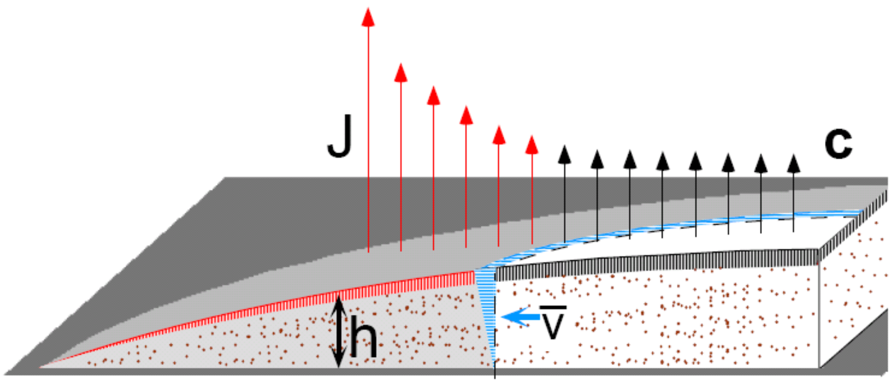
- A syringe pump is used to control the flow of nanoparticle suspension through a needle tip (~100μ inner diameter)
- When a desired amount of liquid is at the tip of the needle the needle is lowered until it contacts the substrate depositing a droplet
- The deposit on the substrate is then taken to an optical microscope for morphological study



Schematic of experimental setup used to create droplets

Droplets of Suspension

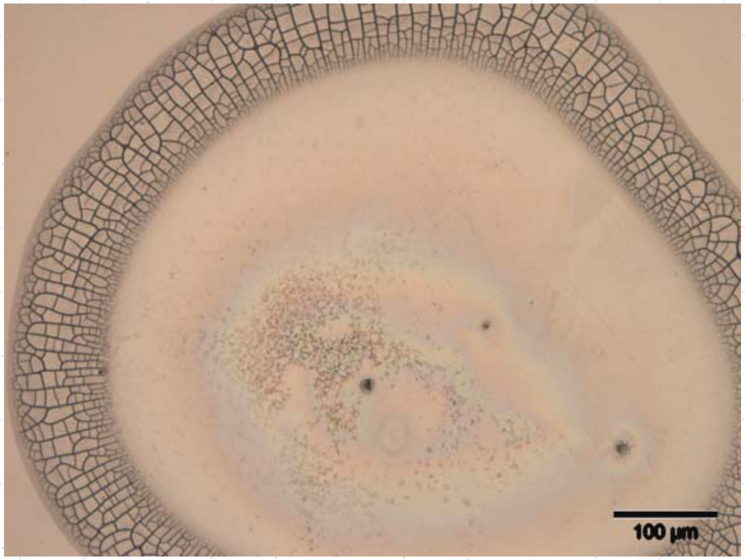
- To determine the effect of geometry, on the morphology of deposits, droplets were created
- Previous papers have described a “coffee stain” effect in droplets of colloidal fluids
- Determine if this “coffee stain” will effect the morphology of our suspension



Dynamics of the “coffee stain” effect. The evaporation rate J is larger at the edge of a droplet due to the curvature of the droplet leading to a flow of fluid and nanoparticles with a velocity v.

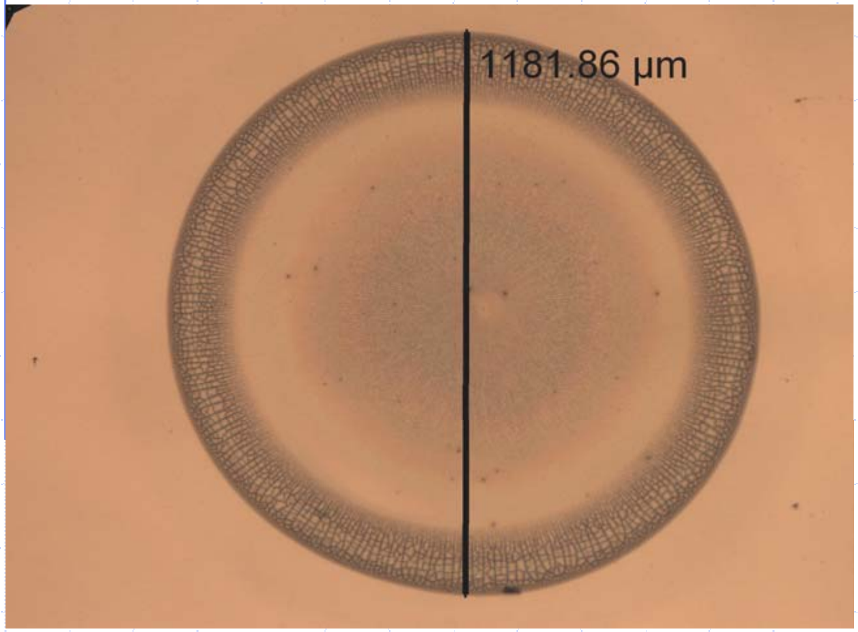
Deegan, R.D., et al, “Capillary Flow as the Cause of Ring Stains from Dried Liquid Drops” , *Nature 389*, 1997

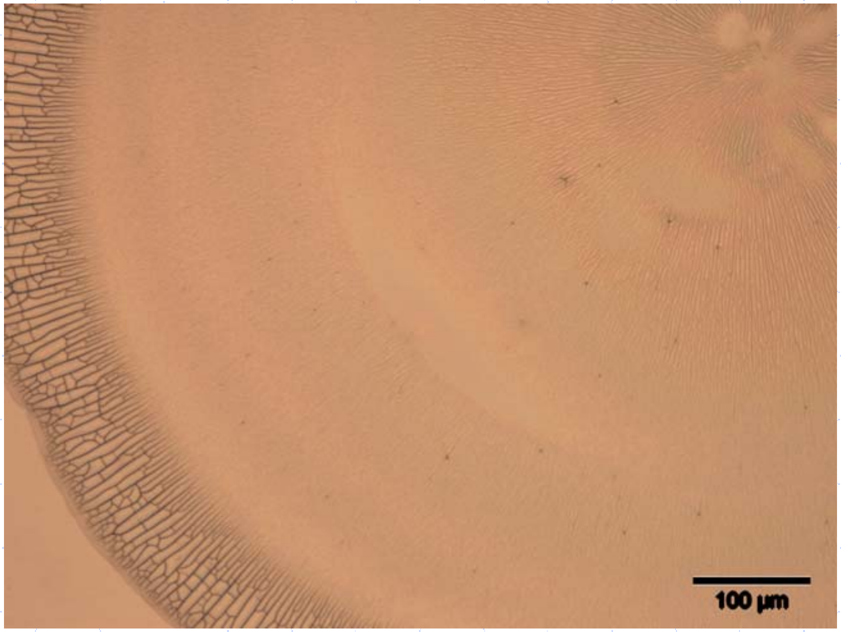
Droplets



Smaller droplets display a noticeable “coffee stain” effect with no visible cracks at the center of the line

Droplets, ctd.

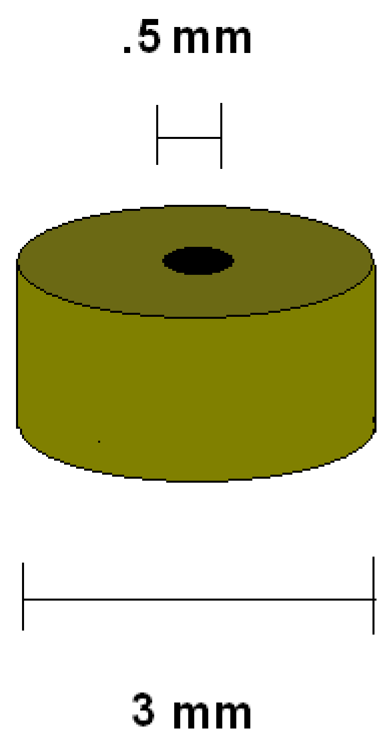




Larger droplets display a “coffee stain” effect, however the larger droplet also contain cracks that go throughout the entire droplet

How to Effect the Morphology of droplets

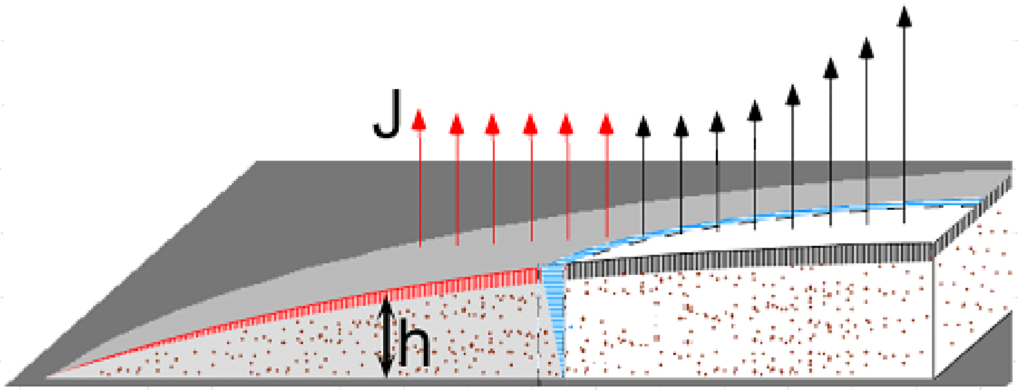
- A cap, with a hole cut into the center, is placed on top of a droplet
- This will saturate the air and alter the way a droplet placed beneath it evaporates
- Two methods were used to place droplets beneath the cap
  - Method one involved the lowering of the needle through the opening until it contacts the substrate
  - Method two involved placing the cap on top of an existing droplet



Drawing of the cap used to effect the morphology of droplet deposits

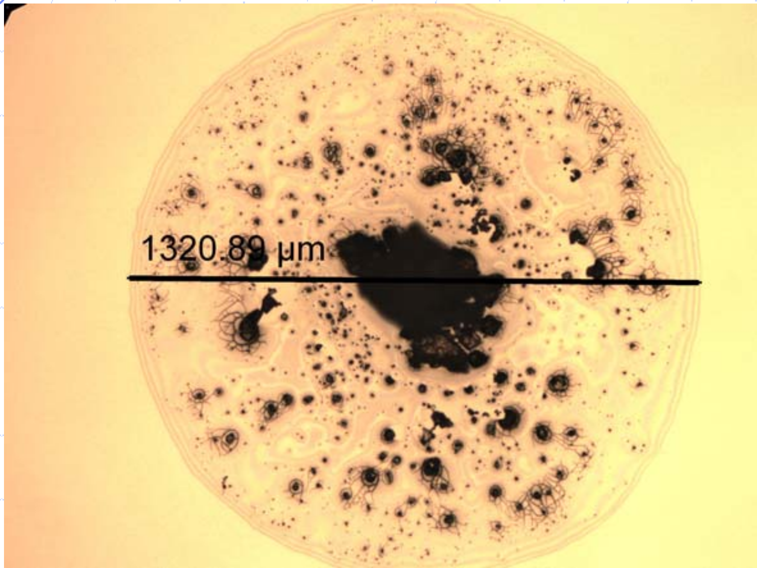
How the Cap Works

- The cap alters the evaporation rate across the entire droplet by saturating the air the droplet is exposed to
- Through adjusting the position of the opening of the cap, relative to the droplet, altered deposit morphologies are formed
  - Morphology of this droplet can then be examined
  - This can be compared to droplets formed with out a cap

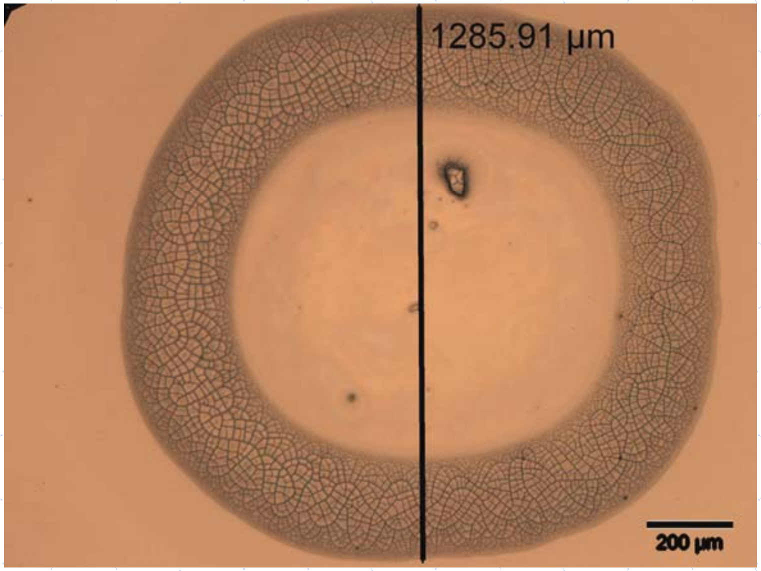


Expected evaporation pattern of droplet under a cap

Results from Cap Experiments



Method one: A droplet placed directly beneath the opening of a cap does not display cracks throughout the entire droplet



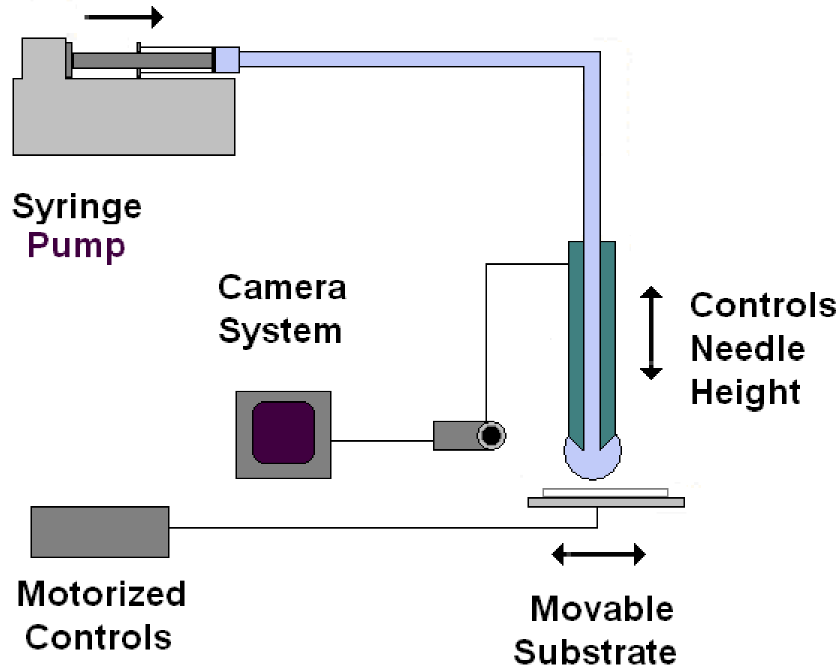
Method two: A droplet not placed directly beneath the opening of a cap displays an altered crack morphology around the edge of the droplet

Droplet Results

- The morphology of droplets are dependent on the size of the droplet
- Droplets were observed to have a “coffee stain” effect
  - This “coffee stain” effect results in an increase in the concentration of the particles at the edge of the deposit
  - This effect was more noticeable on droplets with a diameter of less than 1 mm
- Estimates of the volume of these droplets are unreliable
- Deposits morphology is dependent on the evaporation rate across the droplet
  - Cap experiments show that altering the evaporation rate effects the morphology
  - Two types of morphology are observed depending on how the droplet is placed beneath the cap

Printed Lines Experimental Setup

- A syringe pump is used to control the flow of nanoparticle suspension through a needle tip (~100µ inner diameter)
- The suspension forms a liquid capillary-bridge between the needle and a moveable substrate located underneath and mounted on a motorized platform
- The printed line on the substrate is then taken to an optical microscope for morphological study



Schematic of experimental setup used to create printed lines

Line Printing of Suspension

- Determine the morphology of printed lines
- Determine if printed lines will exhibit a morphology similar to droplets
- Determine if there is “coffee stain” effecting the edges of the printed lines

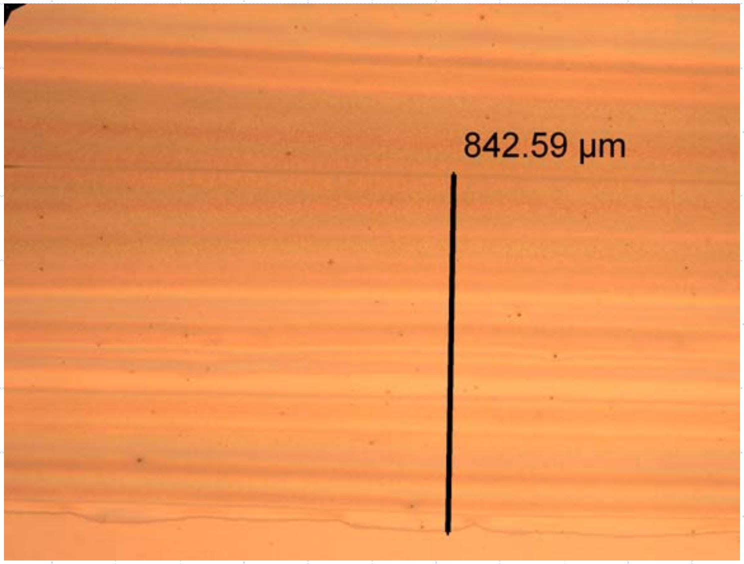


Image of a printed line of a hydrophilic nanoparticle suspension

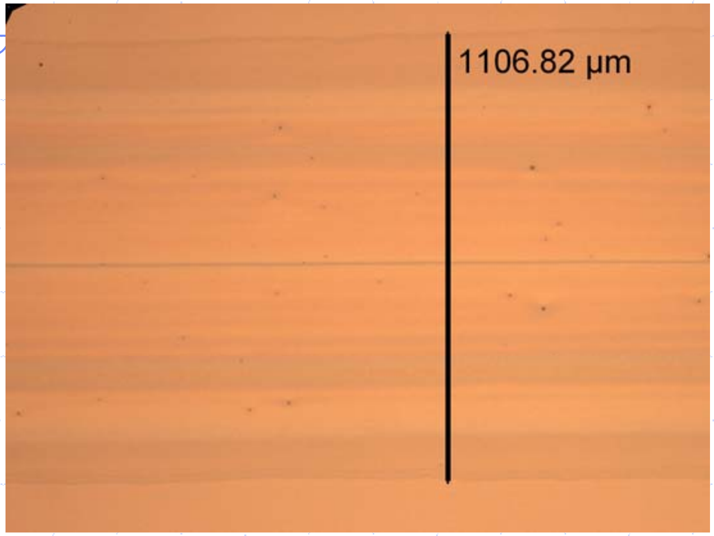
Estimating Layers of Nanoparticle

Flow Rate (ml/hr)	Width of Line (cm)	Height of line (micron)	Diameter of Particle (micron)	Averaged Layers of Particles
0.1	0.1107	0.132992	0.0458	2.903757001
0.3	0.1253	0.352487	0.0458	7.696230648
0.5	0.1624	0.45327	0.0458	9.896733376
1	0.1923	0.765586	0.0458	16.71585544

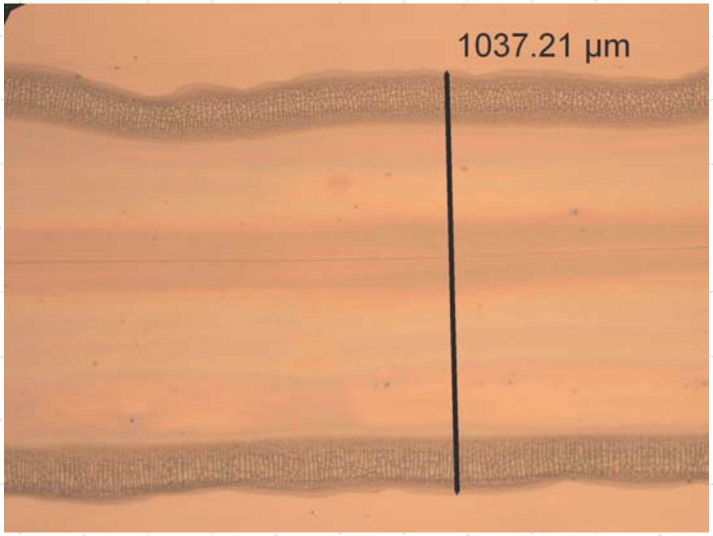
$$H = \frac{Q \times \text{Concentration}}{\text{Width} \times \text{Velocity}}$$

$$\text{Layers of Particles} = \frac{H}{D}$$

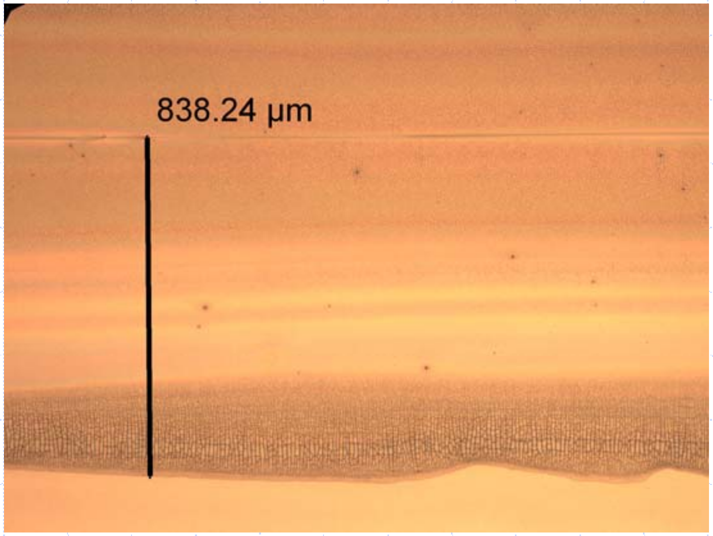
Printed Lines



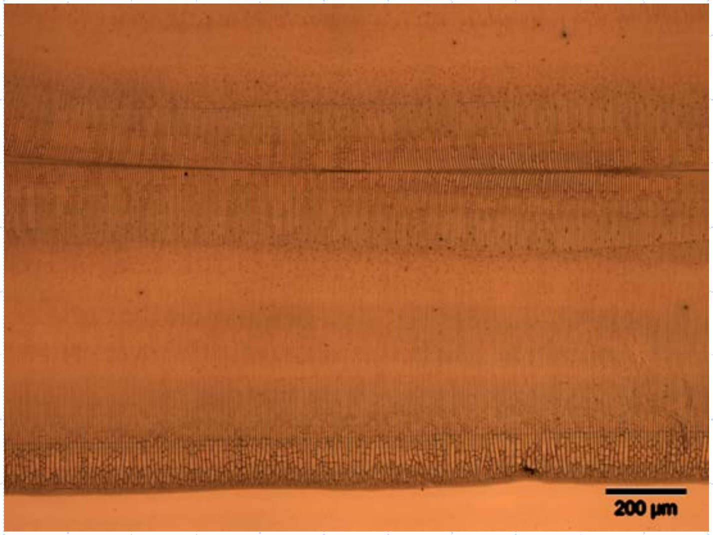
~3 layers no crack development



~8 layers crack development



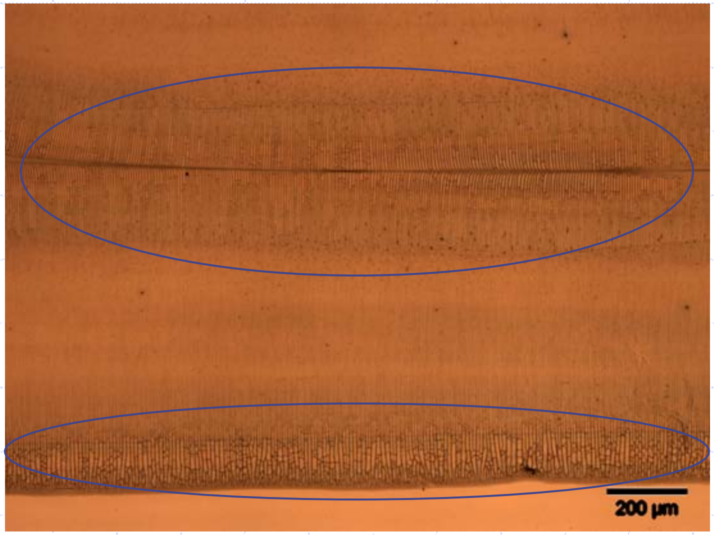
~10 layers crack development



~17 layers crack development

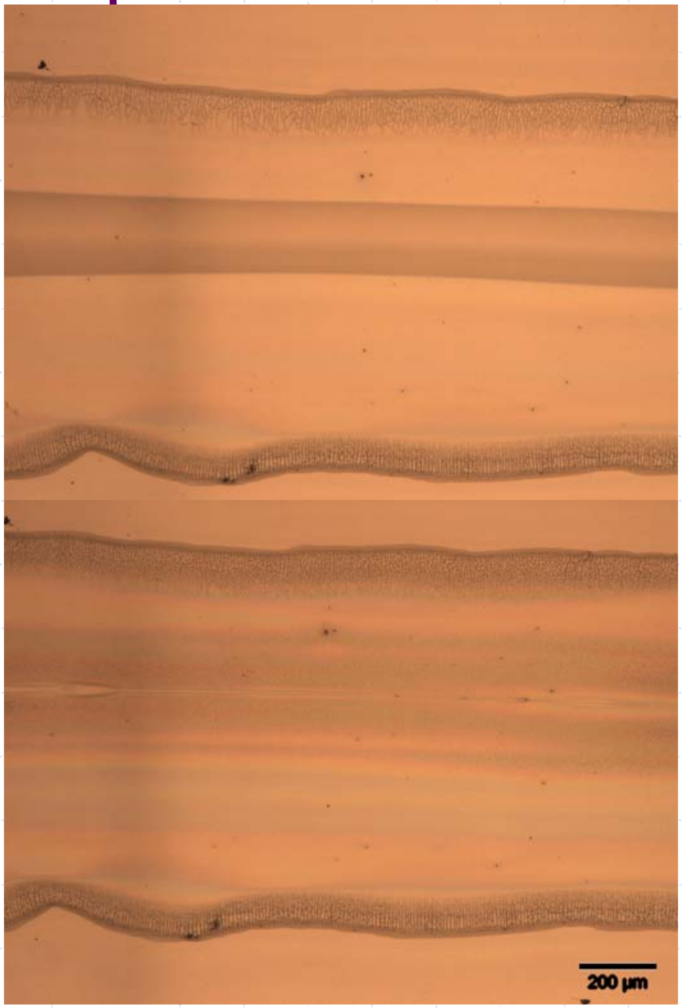
Printed Line results

- Cracking develops when the average number of nanoparticle layers is greater than 8 layers
- Cracking develops all the way through a line when the average number of nanoparticle layers is larger than 17
- Cracking is more prominent at the edges and the center of printed lines



Why Prominent Cracks Develop in the Center

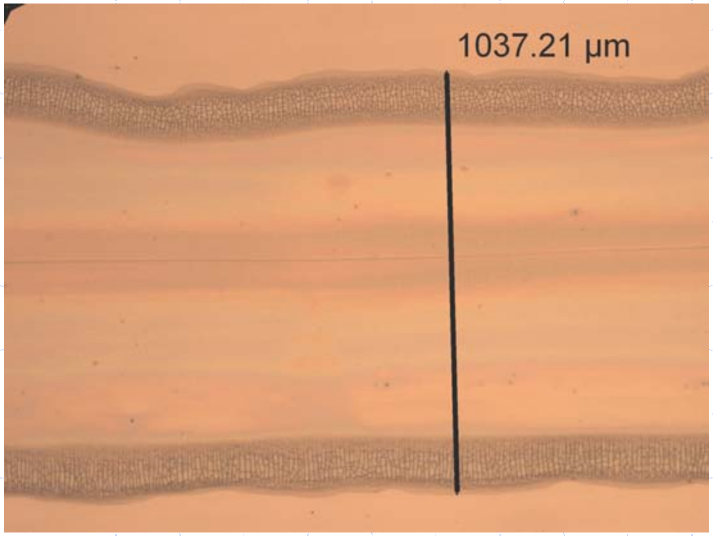
- The contact line must remain pinned
- Observations of printed lines showed that lines were pinned initially for a period of time
- The contact line then becomes unpinned and begins to recede toward the center of the line
- The receding contact line carries nanoparticles and deposits them in the center creating more layers of nanoparticles in the center



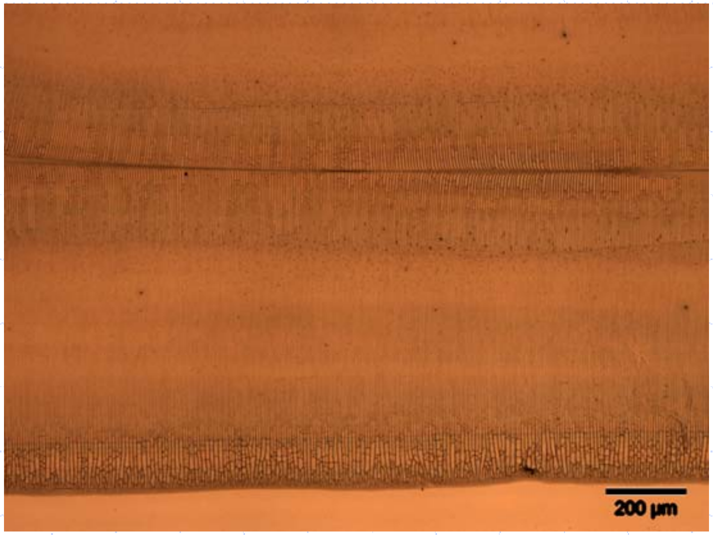
Images of a receding contact line developing cracks at the edges and at the center of the line

Nanoparticle Layers Needed for Cracks to Form

- Cracks develop at the edges when the average number of layers is ~8
- Cracks develop throughout the entire width of the deposit when the average number of layers is ~17
- Because of processes effecting the number of layers present in different areas of the line the number of layers needed to develop cracking is found to be between 8 and 17 layers



~8 layers crack development



~17 layers crack development

Areas for Future Study

- Altering the morphology of printed lines
- Use the understanding gained here to print conductive lines with controlled morphology
- Printing a polymer solution using the novel printing technique of creating a capillary-bridge

Acknowledgements

- National Science Foundation
- Department of Defense
- Manish Tiwari
- Professor Yarin
- Professor Takoudis
- Professor Jursich

References

- [1] Szczech, J.B.; Megaridis, C.M.; Gamota, D.R.; Jie Zhang, "Fine-line conductor manufacturing using drop-on demand PZT printing technology," *Electronics Packaging Manufacturing, IEEE Transactions on* , vol.25, 2002
- [2] Kim, Dongjo; Jeong, Sunho; Park, B.K.; Moon, Jooho, "Direct writing of silver conductive patterns: Improvement of film morphology and conductance by controlling solvent compositions," *Applied Physics Letter*, vol. 89, 2006
- [3] Deegan, R.D.; Bakajin , O.; Dupont, T.F.; Huber, G.; Nagel S.R.; Witten T.A., "Capillary flow as the cause of ring stains from dried liquid drops.". *Nature*, vol. 389, 1997
- [4] Deegan, R.D.; Bakajin , O.; Dupont, T.F.; Huber, G.; Nagel S.R.; Witten T.A., "Contact line deposits in an evaporating drop.". *Physics Review E,* vol. 62, 2000
- [5] Parashkov, R.; Becker, E.; Riedl, T.; Johannes, H.H.; Kowalsky, W., "Large Area Electronics Using Printing Methods," *Proceedings of the IEEE* , vol.93, 2005
- [6] Gratson, G.M.; Xu, M.; Lewis, J.A., "Microperiodic structures: Direct writing of thee-dimensional webs," *Nature*, vol. 428, 2004