

## Variables Impacting Feature Definition of Polyimide using Syringe Based Printing

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### Abstract

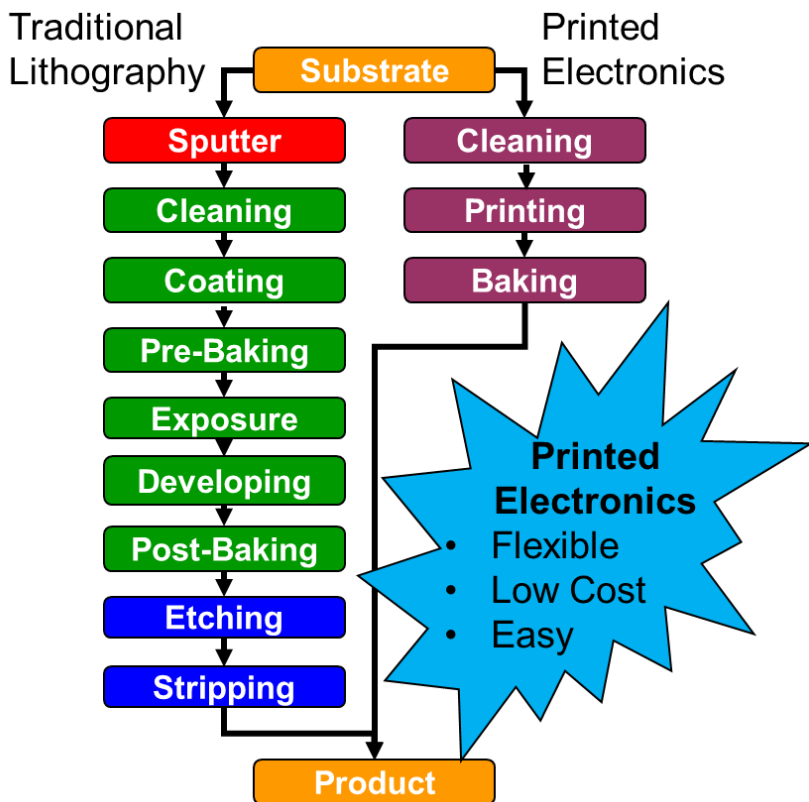
Direct write printing approaches provide an opportunity for additive manufacturing (AM) to impact the electronics industry through cost effective prototyping and manufacturing. Direct write printing of electronics also provides the opportunity for the electronics industry to be impacted by such things as new material research, fewer steps in processing, along with application specific packaging and component configuration. This paper illustrates how process variables affect the feature definition of polyimide film production via syringe deposition printing. This work compares the films as the process variables change, and describes which variables make the greatest impact on feature definition.

### Introduction

The field of printed electronics (PE) is beginning to radically change how macro electronic components are manufactured. Analogous to, yet less mature, than 3D printing of mechanical hardware, PE technologies offer significant benefit over traditional, large volume manufacturing techniques. An example of the type of benefit offered through the PE approach is shown graphically in Figure 1. This figure shows a typical process for applying and patterning a single material layer using a lithographic approach versus a PE approach (Fig. 1). Several advantages are immediately evident from this comparison: For example: (1) many of the very expensive capital equipment factory pieces can be eliminated; (2) tooling needs are also significantly reduced since the printers can be reconfigured digitally (i.e., product specific masks, hard tooling, etc.); and (3) the digital manufacturing environment is highly configurable providing an agile manufacturing environment.

To advance the state of the art in printing of electronic components, the development of printed polyimide capacitors has been undertaken. Capacitors are widely used in most electronic circuits, yet this technology remains largely unchanged for many applications. The focus of this effort is to apply PE technologies to directly print capacitors onto non-traditional surfaces, non-planar surfaces and enhance the capacitance value by directly printing 3-D capacitors. Previous work performed in semiconductor materials <sup>(1, 2)</sup> have shown significant enhancement in capacitance density using etched and plated trench capacitors. These studies have shown enhancement in capacitance density of 16 fF/cm<sup>2</sup> and 9 fF/cm<sup>2</sup>, respectively. This type of

enhancement could radically enhance performance margins and lead to significant reduction in the size of equivalent components. Yet another related and significant area of exploration is to develop the ability to directly print capacitors (and other multi-material) components directly onto non-traditional and non-planar surfaces. Initial work on this project focused on understanding how to apply polymer dielectric films directly onto arbitrary shaped surfaces. Several printing techniques were explored using the syringe based printing discussed.

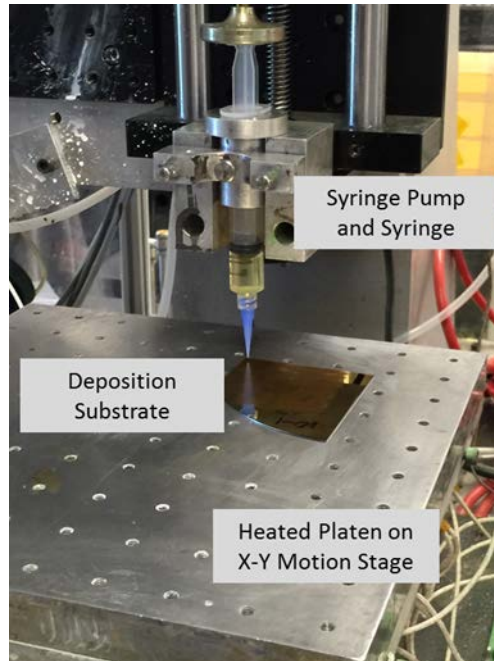


**Figure 1.** Graphical representation showing process steps for applying a single, patterned material layer using traditional lithography versus process steps for applying a single, patterned material layer using a printed electronics approach.

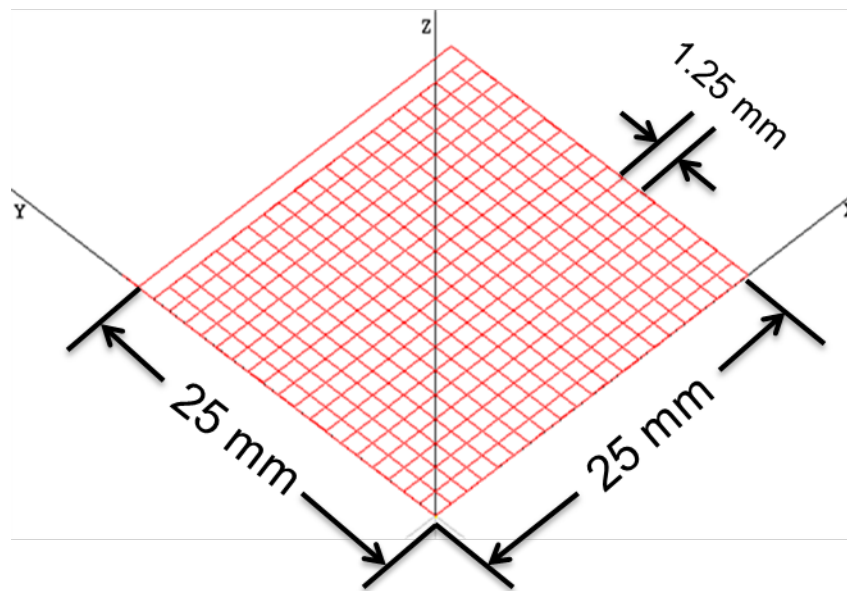
### Experimental Setup

To create uniform films on a surface, it was necessary to work with processes that would allow the film material to remain where it was deposited without flowing away from the deposition area. Syringe dispense was investigated as a method to deposit the films using a small bead of a polyimide solution. For this study, polyimide was chosen as the dielectric material to be deposited due to the extensive material property studies and data available. The fluid is fed to the deposition nozzle using a syringe pump and the volumetric feed rate of the fluid is controlled to ensure that constant output is achieved (Figure 2). A heated platen is used to control the substrate temperature thereby controlling the rate of evaporation of the solvent used in the liquid polyimide. The platen is attached to a computer numerical control (CNC) motion platform to print the film using specific motion pattern. The motion pattern that was used in this

work was designed to deposit a 25 mm x 25 mm square film on the substrate. First a layer of 25 mm lines with a spacing of 1.25 mm between lines was printed in the X direction. Then, a layer of 25 mm lines with the same spacing of 1.25 mm was printed in the Y direction. The two layers together produced a toolpath as shown in Figure 3.



**Figure 2.** Experimental setup used for syringe dispensed printing process.



**Figure 3.** CNC toolpath used to deposit the polyimide film (Red lines illustrate path the syringe tip followed).

The work performed in this study was divided into two sections. First, the initial scoping study focused on changing print variables while keeping the polyimide ink material formulation constant. The material that was used in the initial scoping study was a proprietary formulation of a polyimide precursor in ethanol (UT Dots PI1-AJ). All samples were deposited onto glass slides that were cleaned with acetone immediately prior to deposition. Next, a material study was conducted where the viscosity and surface energy of the polyimide ink was varied to identify which of these variables affected printing definition. To identify which printing variables impacted feature definition of the polyimide, three variables and four conditions for each variable were chosen (Table 1). For this study the tip height (the distance between the syringe nozzle output and the substrate) was varied for each tip orifice diameter and temperature with all other printing parameters being held constant resulting in a total of 64 samples. After the film was deposited, all samples were cured at 150 °C for 30 minutes.

**Table 1.** Process variables used for initial scoping experiment.

<b>Variable</b>	<b>Values</b>			
Temperature (°C)	60	80	100	120
Tip Diameter (mm)	0.25	0.41	0.84	1.19
Tip Height (mm)	0.125	0.188	0.25	0.313

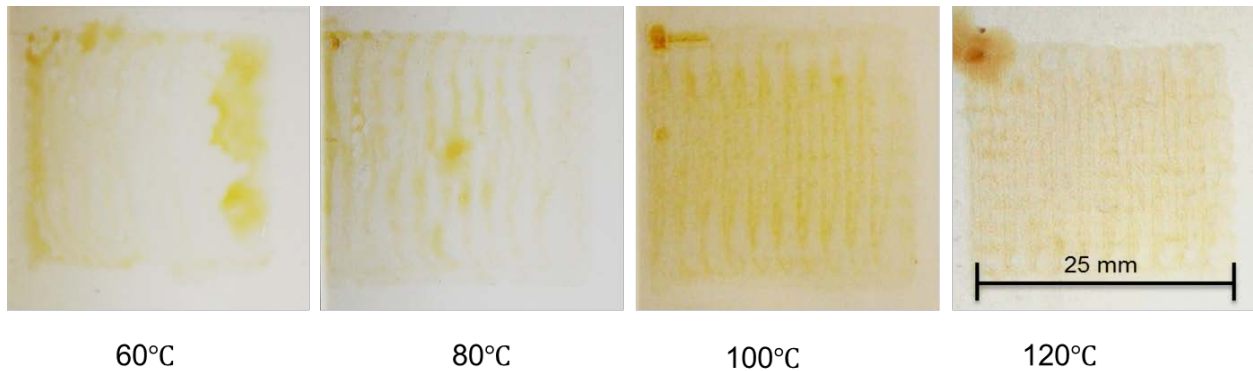
The polyimide ink material used in the second study was a proprietary formulation of polyimide precursor purchased from UT Dots (UT Dots PI-SD2). This ink was diluted with either purified water or ethanol. Again, all samples were deposited on glass slides that were cleaned with acetone immediately prior to deposition. For this second set of samples the variables from the previous study were kept constant, using a platen temperature of 120 °C, tip diameter of 0.25 mm, and a tip height of 0.125 mm above the platen. To understand how print quality varied using either water or ethanol as a solvent with the UT Dots PI-SD2, two sets of ink samples were prepared. Four different dilution formulations were prepared using ethanol and four solutions were prepared using water as the solvent system, (Table 2). A total of 8 samples were printed using these formulations. After the films were deposited, all samples were cured at 150°C for 30 minutes in air.

**Table 2.** Process variables used for secondary viscosity scoping experiment.

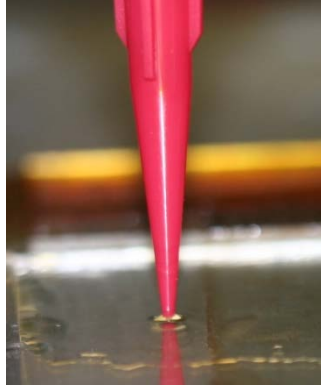
<b>Ink Solution</b>	<b>Dilution</b>			
Water (Polyimide:Water)	1:1	1:2	1:3	1:4
Ethanol (Polyimide:Ethanol)	1:1	1:2	1:3	1:4

## Results and Discussion

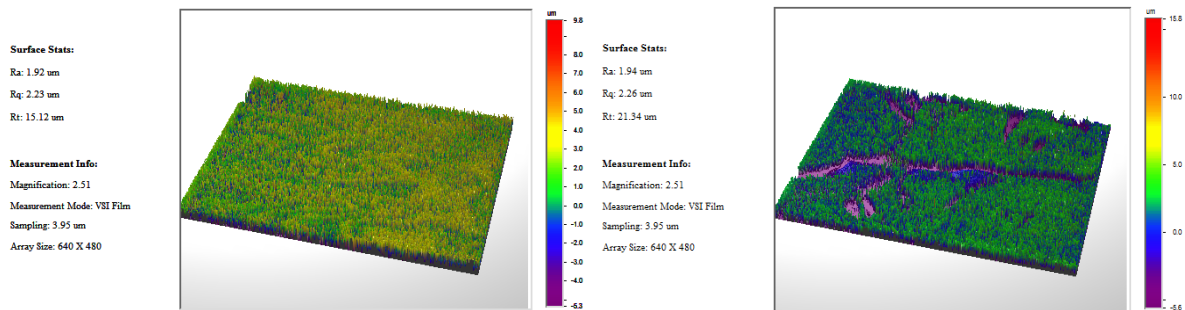
Data collected from the print variable experiments suggest that the temperature of the platen has a large effect on the print quality. Figure 4 shows that samples printed at low platen temperature (60 °C) have material buildup on the right side of the film which is near the final print area. In contrast, images shown in Figure 4 suggest that as the temperature goes up (from left to right), the overall roughness of the film goes down. All of the samples in this figure were printed with a 0.25 mm tip and a 0.125 mm tip height. The image in Figure 5 shows a meniscus forming between the substrate and the syringe tip. The meniscus moves the previously deposited polyimide ink from the desired deposition area until a large portion of the polyimide ink has been relocated to the right hand side of the sample. This relocation of material is the cause of the buildup of polyimide on the right side of the low temperature samples. As the temperature increases the polyimide ink adheres better to the substrate resulting in a more uniform film thickness. It is critical that the polyimide ink remains where it is deposited as the process transitions from printing on planar to nonplanar 3D surfaces. Figure 6 shows that the root mean square surface roughness ( $R_q$ ) of both the high temperature and low temperature are very similar. The high temperature samples have a thicker film, which is expected because the material is not being pushed from to the right side edge of the sample.



**Figure 4.** Optical images of how the temperature changes film quality. From left to right, 60 °C, 80 °C, 100 °C and 120 °C. All other parameters held constant.

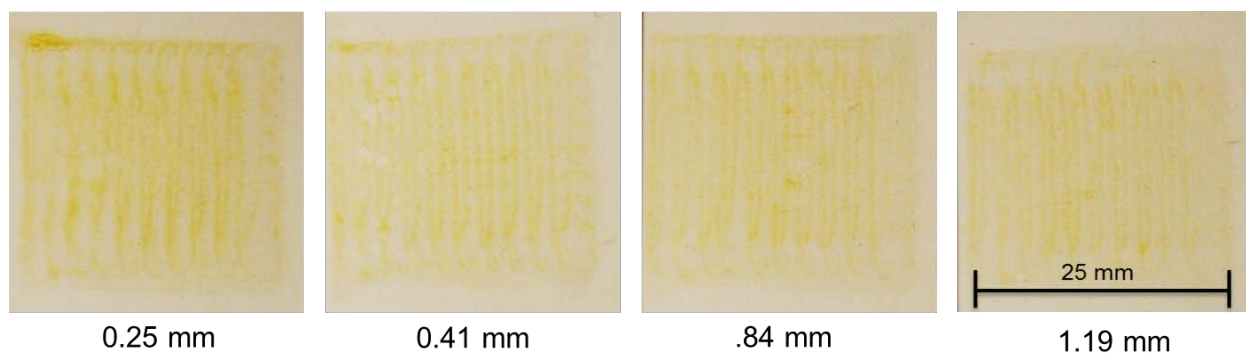


**Figure 5.** Images of how meniscus forms between syringe tip and substrate. The meniscus pushes polyimide ink around the substrate when the platen is at the lower temperatures. (60 °C shown)



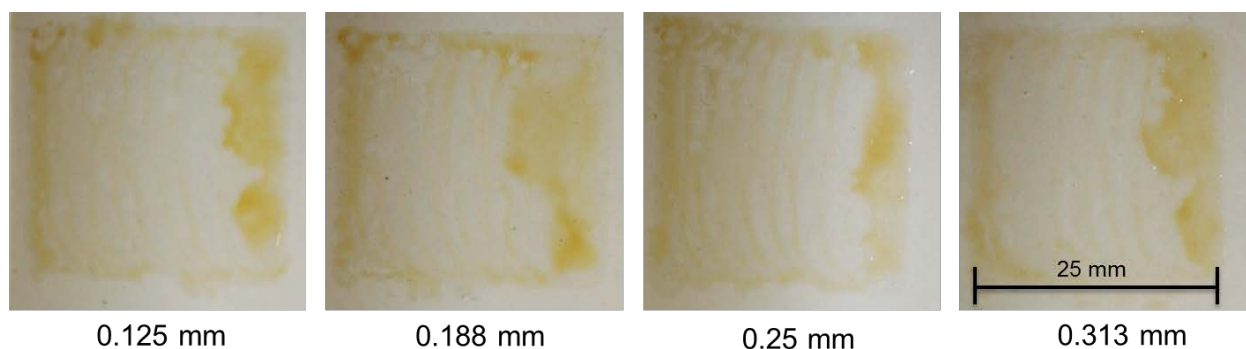
**Figure 6.** 3D film thickness measurements with WYKO optical profilometer. From left to right, 60°C, and 120°C. All other parameters held constant.

In many AM processes the tip diameter plays an important role in the print quality due to the direct correlation between surface finish feature build resolution. However, with the UT dots PI1-AJ polyimide, the effect of varying the tip diameter is not evident. For example, in Figure 7 Platen temperature and tip height were held constant at 120 °C and 0.125 mm, respectively while the tip diameter was varied. Yet, the images in Figure 7 show no discernable difference in the film quality as tip diameter is varied. Similar results were observed at all other temperatures and tip heights.

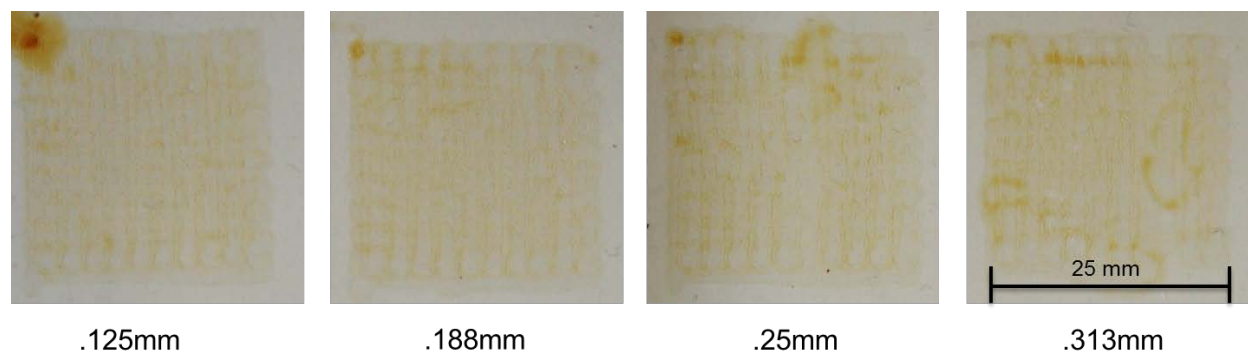


**Figure 7.** Optical images of how the tip diameter changes film quality. From left to right, 0.25mm, 0.41mm, 0.84mm, 1.19mm. All other parameters held constant.

Results would suggest that tip height has a more significant effect on print quality. Figure 8 shows four samples printed using a 60 °C platen temperature and a tip diameter of 0.25 mm. As the tip height was increased the print quality, film thickness and feature definition remained unchanged. Figure 9, shows four samples printed using a platen temperature of 120 °C and a tip diameter of 0.25 mm. In the samples printed at the higher temperature, the tip height became more important. At the lowest tip height the syringe was able to deposit a very thin and much more uniform film. As the tip was raised, it was observed that the polyimide ink would form a ball on the end of the tip, causing the ink to pull away from the print substrate. As the drops increased in diameter, the drops would intermittently contact the print substrate producing rings of built up material on the sample.

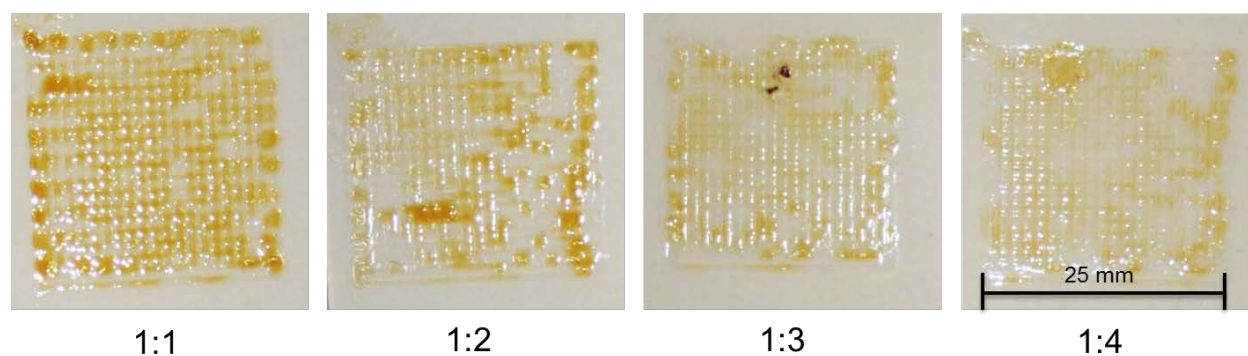


**Figure 8.** Optical images of how the tip height changes film quality at low temperature. From left to right, 0.125mm, 0.188mm, 0.25mm, 0.313mm. All other parameters held constant.



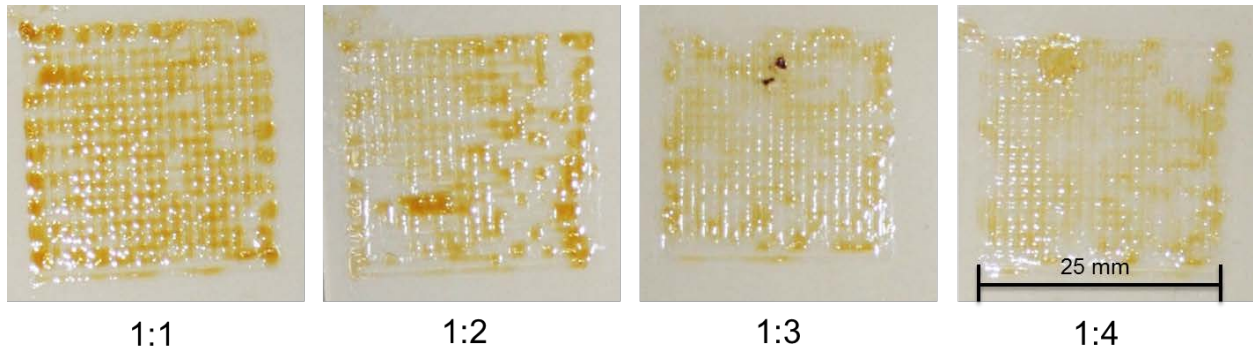
**Figure 9.** Optical images of how the tip height changes film quality at high temperature. From left to right, 0.125mm, 0.188mm, 0.25mm, 0.313mm. All other parameters held constant.

Results from the second study focused on material variations, suggest that both viscosity and solvent type affect printed film quality. Since smooth consistent films, irrespective of surface orientation are needed, it is important that the ink be optimized to allow printed lines to flow together to create a uniform, smooth film while those lines remain pinned to the print location. In Figure 10 there are 4 samples that were printed with different dilutions of water. It is observed that the more concentrated polyimide ink resulted in taller lines which were pinned to the print location. As the dilution of the ink increases the film becomes smoother and more uniform. Figure 11 shows samples printed using ethanol in place of water as the diluent. Similar results are observed where the film becomes smoother and more uniform as the viscosity decreases.



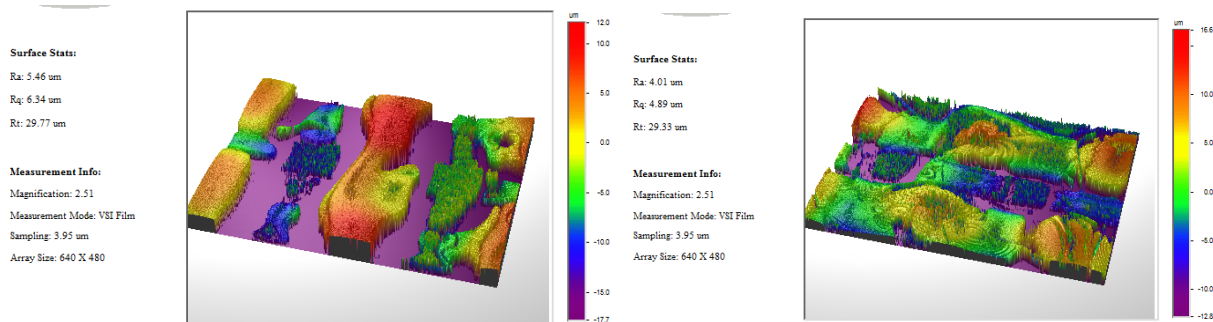
**Figure 10.** Optical images of how the viscosity of the material changes film quality. From left to right, (Polyimide:Water) 1:1, 1:2, 1:3, 1:4. All other parameters held constant.





**Figure 11.** Optical images of how the viscosity of the material changes film quality. From left to right, (Polyimide:Ethanol) 1:1, 1:2, 1:3, 1:4. All other parameters held constant.

It is evident from the samples shown in Figures 10 and 11 that the solvent used for diluting the polyimide ink changes how the material flows. Figure 12 shows images from 3D film thickness measurement of the 1:1 samples that were shown in Figures 10 and 11. In both images the purple color represents the glass substrate that the samples were printed on, and holes in the film. The images reveal when the ink is diluted with water, beads of material that were deposited do not flow together leaving large areas void of polyimide. However, when the polyimide is diluted with ethanol the ink more readily wets the slide leaving fewer holes in the film. This results in a smoother and more uniform film than was printed with the water diluted ink.



**Figure 12.** 3D film thickness measurements with WYKO optical profilometer. From left to right, water and ethanol both at a 1:1 dilution. All other parameters held constant.

## Conclusions and Future Work

This work compares variables that impact feature definition when using a syringe based deposition of polyimide ink. From the parameters that were studied, the smoothest most defined film can be achieved using a platen temperature of 120°C, tip diameter of 0.250mm, tip height of 0.125mm, UT Dots PI-SD2 ink in a 1:4 dilution with ethanol. Since deposition on conformal surfaces is desired, future work should include understanding and exploring additional options to exploit surface energy to promote wetting between print lines and material pinning in the print location.

## References

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2. M. Detalle, M. Barrenetxea, P. Muller, G. Potoms, A. Phommahaxay, P. Soussan, K. Vaesen, W. De Raedt, “High density, low leakage Back-End 3D capacitors for mixed signals applications”, *Microelectronic Engineering* **87** (2010) 2571–2576