Low-Cost and Robust Printing of Resistance Thermometer Sensors Using the Voltera

ENGR 241 Project Report

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1. Introduction

Sensor networks utilize an array of distributed sensors to monitor and control a system. They can be found in many applications, from robotics to structural health monitoring to internet-of-things (IoT) technology. These networks can be as small as a glove, and as large as an aircraft wing.

1.1 Problem Statement

One significant challenge with sensor networks is the ability to scale up to large area applications. Traditional manufacturing techniques used in the semiconductor industry are expensive and difficult to scale up to cover large surface areas. Research in more novel techniques like screenprinting [1] and stretchable networks [2] show promising results, but suffer from durability issues at the interconnects. Additive manufacturing, also known as 3D printing, offers a cost-effective way to rapidly prototype and produce sensors. 3D printed capacitive, piezoresistive, and thermoresistive sensors, among others, have been demonstrated in literature [3]. As an umbrella term, 3D printing represents many manufacturing techniques all based on an “additive” process, where material is added in a step-by-step process. The Voltera V-One uses a direct-write process, where both high viscosity conductive ink and solder paste can be directly injected and deposited onto a substrate. The deposited ink is annealed by the heated bed integrated into the machine. Deposited solder paste is reflowed using the same heated bed. By integrating sensors and interconnects into one manufacturing process, a low-cost, durable sensor network can be achieved.

1.2 Objective

This project will look at fabricating and testing Resistance Temperature Detector sensors (RTD) in order to characterize useful parameters for sensor network printing in the future using the Voltera V-One. To do so, characterization of the printed ink will be required. We will look at the geometric properties of the printed ink as well as its resistivity as a function of temperature.

2. Experimental Plan

2.1 Equipment and Materials

2.1.1 SNF/ExFab Equipment

- Voltera V-one

2.1.2 Non-SNF/ExFab Equipment

- Probe station (Senesky lab)
- Semiconductor parameter analyzer (Senesky lab)

2.1.3 Materials

- Voltera conductive silver ink
- Voltera flexible silver ink[1]
- Voltera ink cartridges
- Elastomer (dragon skin)
- Borosilicate glass slides
- Creative Materials inks; see Section 2.2.1.2

2.2 Experimental Plan

2.2.1 Independent Variables

2.2.1.1 Substrates

We chose the following substrates during the downselection process.

- borosilicate glass
- Kapton (polyimide)

[1]https://www.voltera.io/store/product/?productId=Z2lkOi8vc2hvcGlmeS9Qcm9kdWN0Lzk3NzExMzI0ODE=

2.2.1.2 Inks

We chose the following inks during the downselection process.

- Voltera Conductive (silver)
- Voltera Flexible (silver)
- Creative Materials 118-41 Solvent-resistant electrically conductive ink (silver, viscosity 18 Pa-s, can be thinned with solvent, 0.01 Ohm/sq/mil sheet resistance)[3]
- Creative Materials Exp-2649 Flexible High Temperature Electrically Conductive Ink (silver, viscosity 12-17 Pa-s, can be thinned with solvent, silicone based, 0.35 Ohm/sq/mil sheet resistance)

Note: For maximum shelf life, Voltera inks should be refrigerated, and Creative Materials kept at -10°C.
Note: The Creative Materials inks are deemed toxic due to the solvents (see MSDS), and therefore should be used in the fume hood, and waste must be bagged and disposed of properly

2.2.1.3 Process Parameters

The following process parameters were identified from a larger space of settings[2]. They were chosen because we believe they have the highest impact on the dependent variables.

- Anneal temp: [Recommended temp, Higher than recommended temp]
- Nozzle Sizes: 225um, 150um and 100um

2.2.2 Dependent Variables

2.2.2.1 Geometry

- Width and thickness of printed lines
- Morphology and print quality

2.2.2.2 Conductivity

- At room temperature and elevated temperatures up to 200°C or the substrate maximum operating temperature (whichever is lower)
- Characterization will be done using the high-temperature probe station and semiconductor parameter analyzer in Professor Senesky's lab

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[2] https://support.voltera.io/hc/en-us/articles/360000822694-Print-Settings-Overview

2.2.3 Design of Experiments Table

Ink	Substrate	Nozzle Size (um)	Anneal Temp (C)
Voltera Conductive	Glass	150	220
Voltera Conductive	Glass	150	300
Voltera Conductive	Glass	100	220
Voltera Conductive	Glass	100	300
Voltera Conductive	Kapton	150	300
Voltera Conductive	Kapton	150	220
Voltera Conductive	Kapton	100	300
Voltera Conductive	Kapton	100	220
Voltera Flexible	Glass	150	155
Voltera Flexible	Glass	150	200
Voltera Flexible	Glass	100	155
Voltera Flexible	Glass	100	200
Voltera Flexible	Kapton	150	155
Voltera Flexible	Kapton	150	200
Voltera Flexible	Kapton	100	155
Voltera Flexible	Kapton	100	200
CM EXP-2649	Glass	225	150
CM EXP-2649	Glass	225	200
CM EXP-2649	Kapton	225	150
CM EXP-2649	Kapton	225	200
CM 118-41	Glass	225	175
CM 118-42	Glass	225	220
CM 118-43	Kapton	225	175
CM 118-44	Kapton	225	220

The samples produced from this table are shown in Figure 1, with a few exceptions due to damaged samples, melted substrates, and sensor shorts.

3. Resistance Temperature Measurements

3.1 Measurement Process

In order to compare our selected input parameters' effects on RTD sensors, we measured the Resistance-Temperature curve of each sample. By placing the samples on a hotplate, measuring the temperature with a thermocouple (resolution 0.1°C), and measuring resistance with a voltmeter (resolution 0.1 Ohm) at 20°C increments (see Figure 2). The R-T curves for each sample are shown in Figure 3 below.

Our DoE included testing each sample at the recommended temperature by the ink manufacturer, as well as at a higher temperature. In the cases of the Kapton substrate with conductive ink, the recommended temperature was already 220°C (high for Kapton). The second higher temperature of 300°C was high enough that it melted the Kapton substrate, and those samples were discarded.

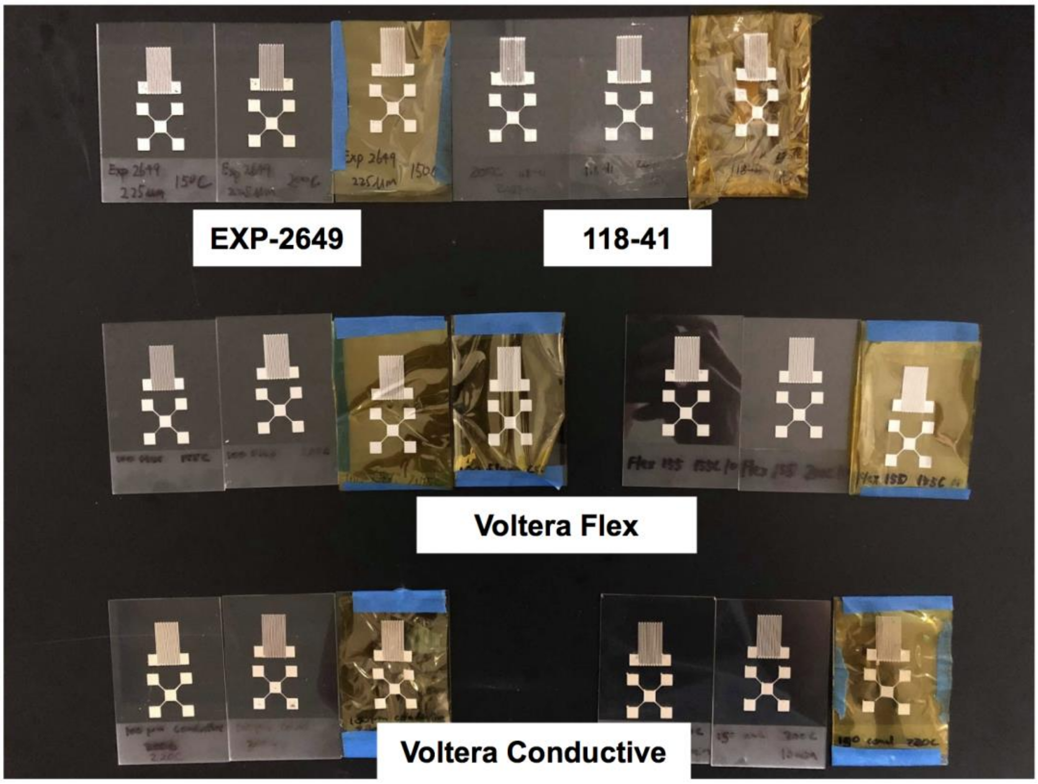
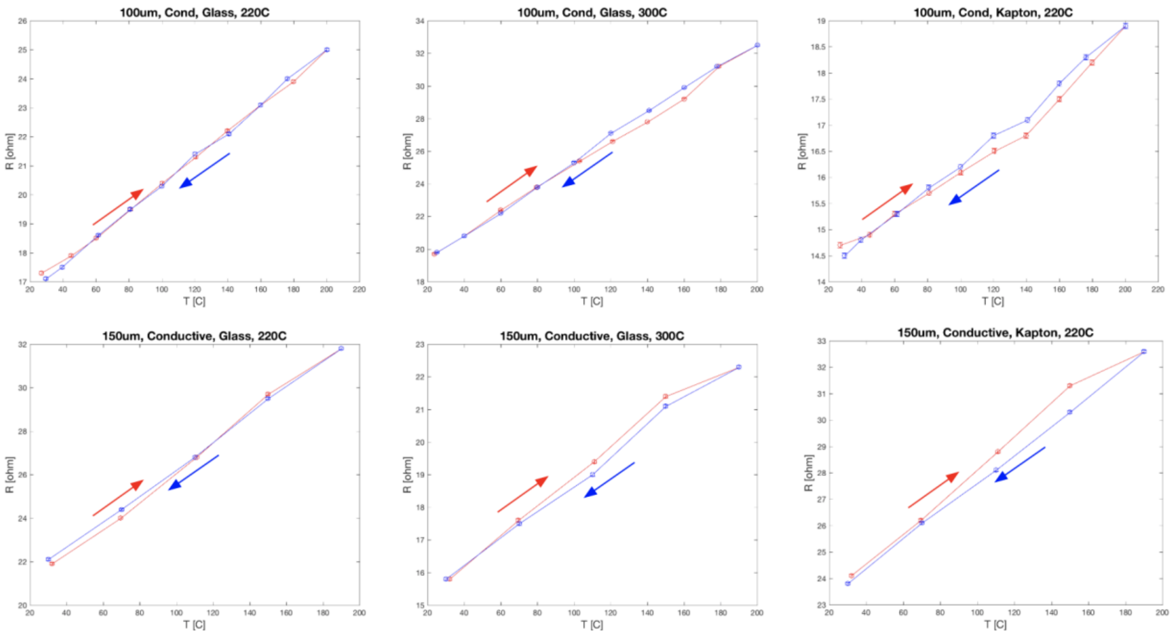


Figure 1: Final samples produced, arranged by ink. Some samples are missing because of disconnects that prevented RTD testing, and because the DoE high annealing temperature melted the Kapton substrate

Figure 2: Experimental setup for measuring the Resistance-Temperature curves of the RTD sensors.

3.2 Resistance-Temperature Data

We noticed hysteresis in the R-T curves for most samples; however, we suspect that this may be due to the fact that the samples are annealing further during the heating test. Hysteresis persisted in samples that we measured for up to 4 cycles. After hundreds of cycles, material may fully anneal and this hysteretic effect reduced or even eliminated. Future work could involve running the sensors for many cycles to see if this is improves their performance in this way.



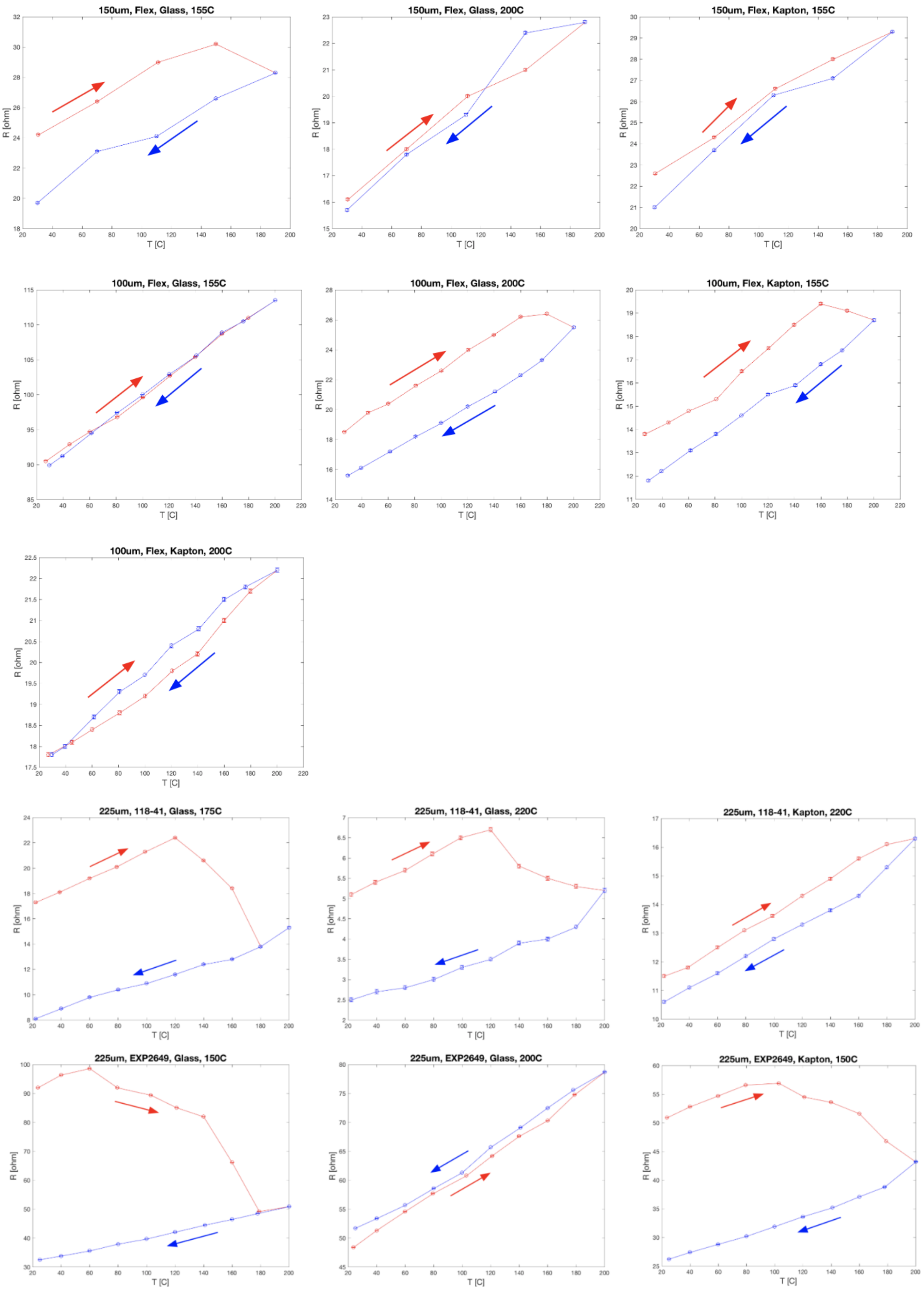


Figure 3: Plots of R-T curves for all samples measured. Red denotes increasing temperature, blue denotes decreasing temperature

3.3 Effects of Anneal Temperature

Annealing the inks is a necessary step to bake off the solvent, thus bringing the conductive particles closer together and increasing conductivity (see Figure 4). The temperature and time period that the inks are annealed at affects how much solvent burns off. For our experiments, we always baked an ink at the manufacturer's suggested temperature and time period, as well as at a higher temperature.

It is clear from the plots in Figure 3 above, (of which is expanded in Figure 5 below) that the samples need to be annealed at a temperature greater than the sensor's maximum operating temperature. Figure 5 shows that the temperature increase to 200°C for the 155°C annealed sample substantially lowers the sensor resistance because the conductive ink has now been further annealed, thus decreasing resistance of the sensor.

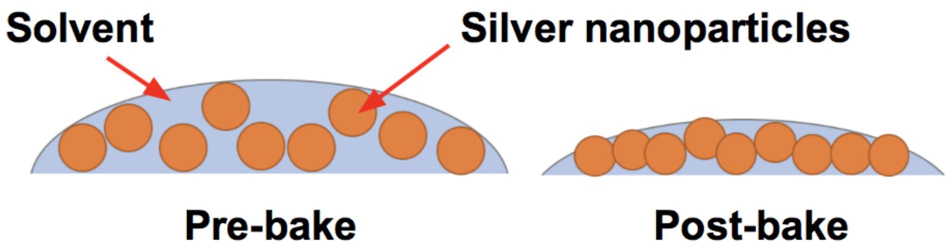


Figure 4: Depiction of how conductivity increases as solvent particles are baked off at higher annealing temperatures and time period

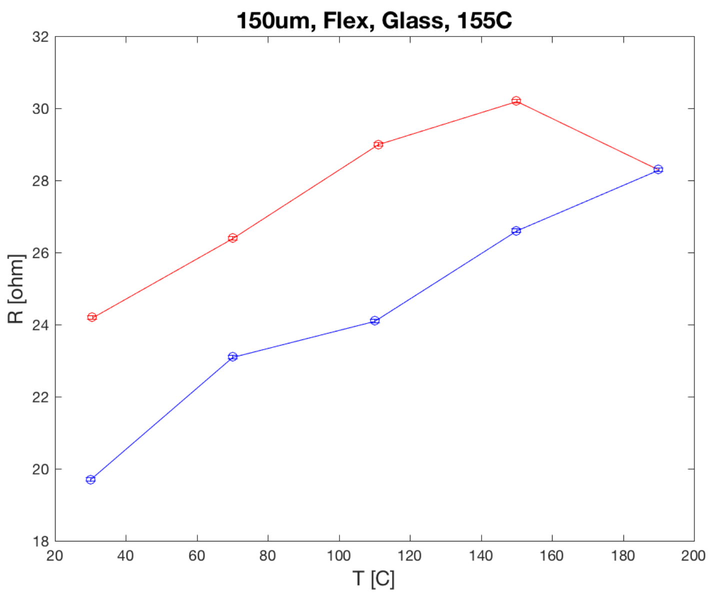


Figure 5: One of the plots from Figure 3. The 155C cure temperature samples exhibit an especially large hysteresis loop

3.4 RTD Sensitivity

The sensitivity of the RTD is defined as the sensor resistance change in response to the temperature change. There are two ways to represent the RTD sensitivity. The first definition is denoted by Equation (1). It indicates an absolute value change in resistance for each ℃. This sensitivity is dependent on the RTD geometry as well as its material.

$$\frac{\Delta R}{\Delta T} \text{ (Unit: Ohm / ℃)} \tag{1}$$

However, in this project, we are interested in comparing the sensitivity data through all 4 inks in our DoE table. Therefore, we utilized a second definition of RTD sensitivity which is denoted by equation (2). It indicates the percentage change with respect to the reference resistance for each ℃. This sensitivity is only dependent on the sensor material.

$$\frac{\Delta R / R_o}{\Delta T} \text{ (Unit: % / ℃)} \tag{2}$$

Therefore, by using the second definition, we obtained sensitivity data for 4 inks we tested (see Figure 6). The Voltera flexible ink gives the lowest sensitivity value; the Creative Materials EXP-2649 ink shows the highest value, which is comparable to the standard, platinum based RTD sensor whose sensitivity is 0.385 % / ℃.[3]

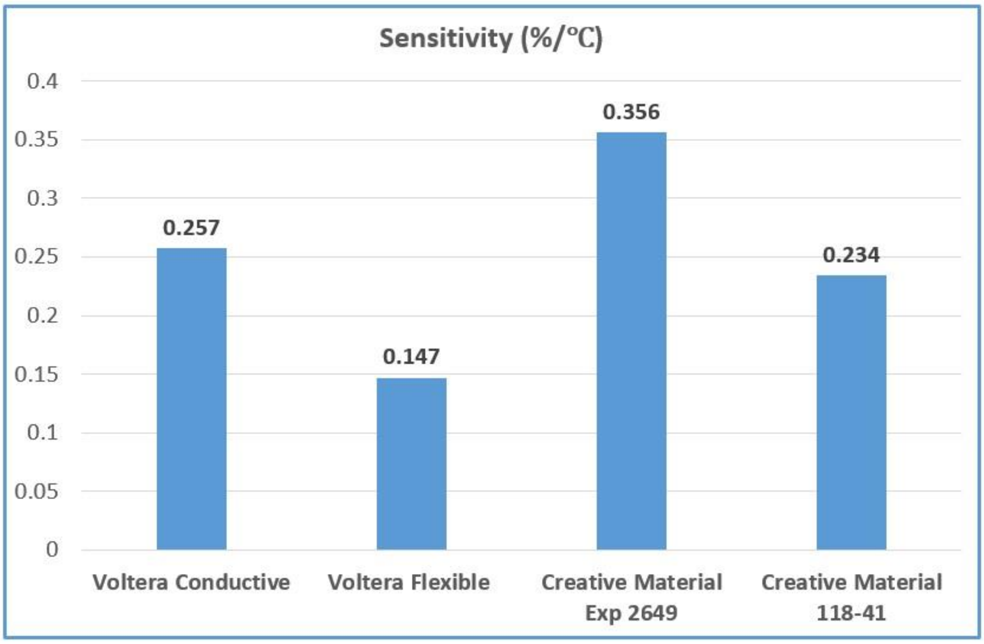


Figure 6: Sensitivity data for all 4 inks

[3] https://instrumentationtools.com/what-is-rtd-sensitivity/#.Wxr5zvZFw2w

4. Sheet Resistance Measurements

4.1 Introduction

Sheet resistance is a measure of the resistance of a flat 2D sheet of material. This value only depends on the bulk resistivity of a material and the thickness of the sheet. The relationship between resistivity *ρ*, sheet resistance R_s, and the resistance *R* are given in equations (3) and (4).

$$R = \rho \frac{L}{W \cdot t} \tag{3}$$

$$R_s = \frac{\rho}{t} \tag{4}$$

Because resistivity is solely a material property, it is an important parameter for the design of circuits and resistive elements on the Voltera. This section will present our results and analysis on sheet resistance and resistivity measurements.

4.2 The van der Pauw Method

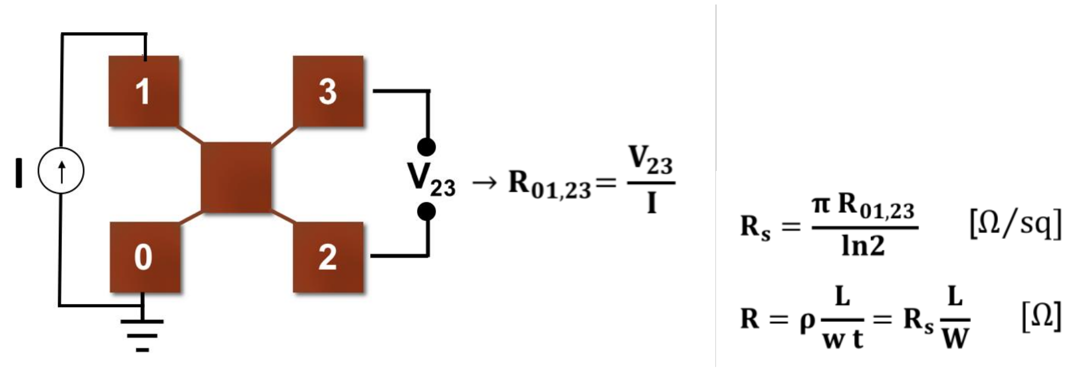


Figure 7: The van der Pauw test structure

The van der Pauw method [4] is a technique to measure the sheet resistance of a flat 2D material. Key assumptions of this technique are that the specimen to be measured is:

- Flat with uniform thickness
- Free of holes
- The material is homogeneous and isotropic
- Contacts used to inject current and measure voltage on the specimen should be at least an order of magnitude smaller than the specimen itself

To calculate the sheet resistance, a van der Pauw test structure (shown in Figure 7) is printed onto the substrate. The center square is the area of interest--the four surrounding squares are simply pads that make it easier to connect probes and don't significantly affect the measurement. A current *I* is injected into pad 1 and leaves through pad 0 (ground). The voltage difference V_{23} (defined as V_3 - V_2 with respect to ground) between pads 3 and 2 is measured. Assuming the center structure is indeed a square, the sheet resistance can be calculated using a simplified form of van der Pauw's equation:

$$R_{01,23} = \frac{V_{23}}{I} \tag{5}$$

$$R_s = \frac{\pi R_{01,23}}{ln(2)} \tag{6}$$

Using equation (4), the resistivity can be calculated from the sheet resistance.

4.3 Assumptions and Limitations of Measurement

The four requirements listed in Section 4.2 are not fully met by our specimens. Out of these four assumptions, the first three are questionable due to defects in the printing process.

The thickness of our samples is not well controlled, due to the difficulty in printing samples with consistent thickness. This is due not only to the printing process itself, but also the calibration process. The recommended procedure for calibrating print quality on the Voltera involves printing calibration lines (shown in Figure 8) and comparing the output visually to a reference. This is highly qualitative and yields specimens with a different thickness on every print. Future work could focus on developing a more quantitative technique to calibrate and control the thickness of prints.

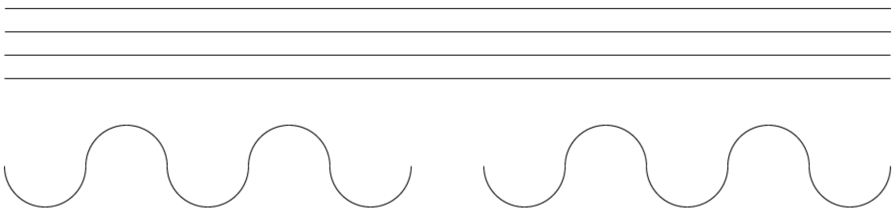


Figure 8: A calibration curve similar to this is used to visually calibrate nozzle height and flow rate.

In addition, the printed material is not expected to be isotropic and homogeneous, due to voids and gaps in the print, as seen in Figure 9. However, the van der Pauw measurement will still yield an average sheet resistance value, which will be useful for designers.

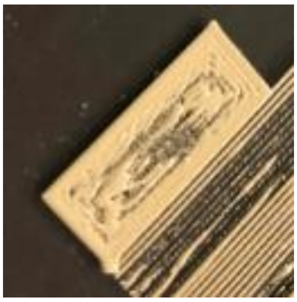


Figure 9: A severe case of voids and gaps in a print. Most prints are not this terrible, but will still show signs of anisotropy.

4.4 Test Setup

Specimens were measured using a Keysight B1500A Semiconductor Parameter Analyzer. Current was swept from 0 to 100 mA in 2 mA steps and voltage measured to generate an I-V curve. Measurements were taken at room temperature and at 170°C on a custom Signatone probe station with a heated chuck, as shown in Figure 10. A linear fit was applied to the I-V curve to determine $R_{01,23}$.

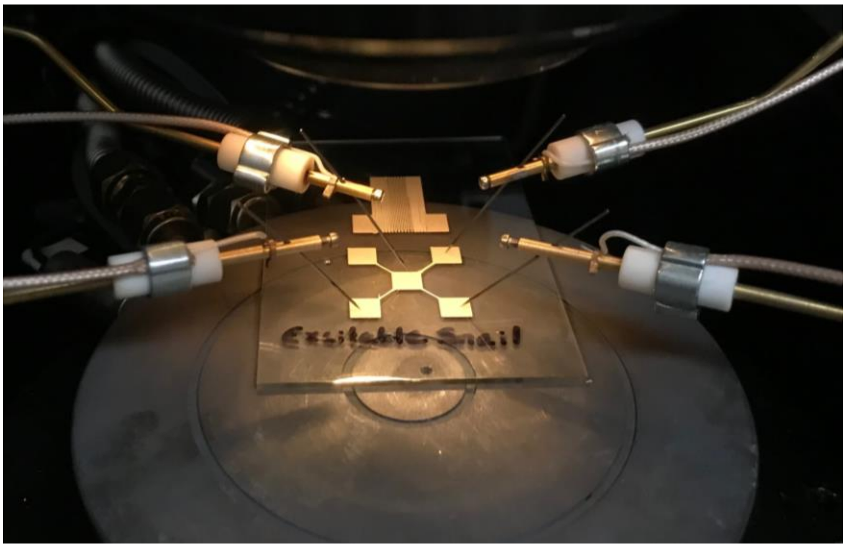


Figure 10: 4 point probing a sample for sheet resistance at room temperature and at 170°C; Excitable Snail is the name of the batch of ink Voltera sent

4.5 Results and Analysis

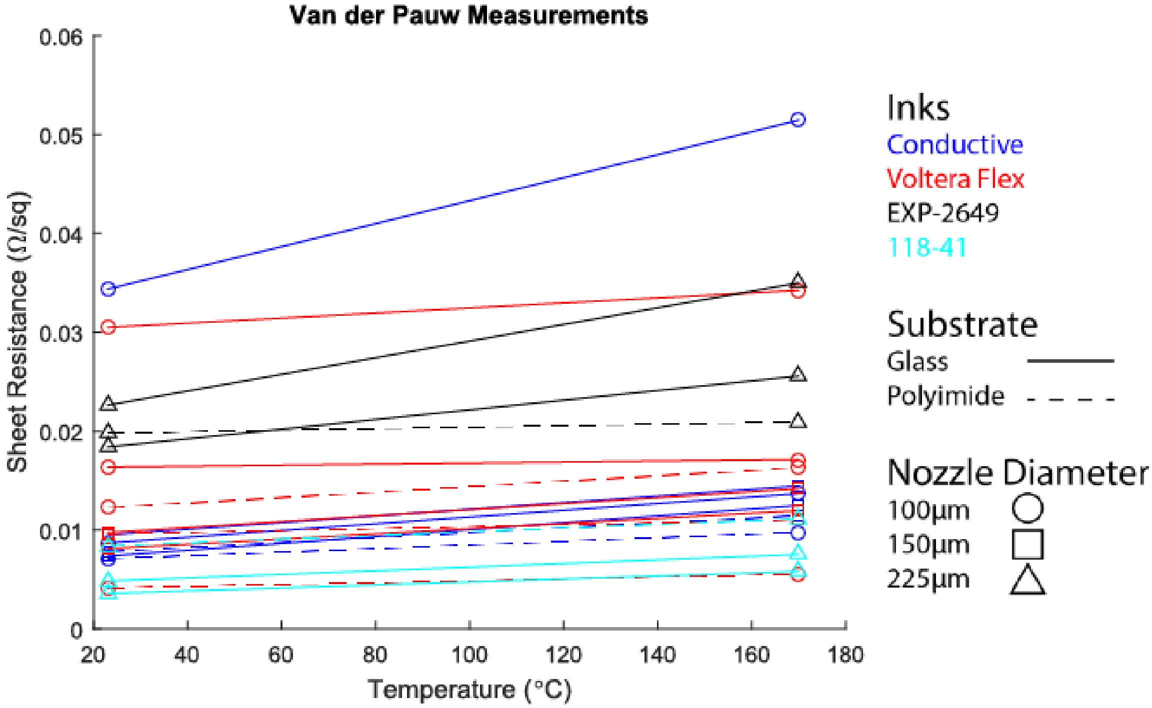


Figure 11: Sheet resistance of specimens as a function of temperature.

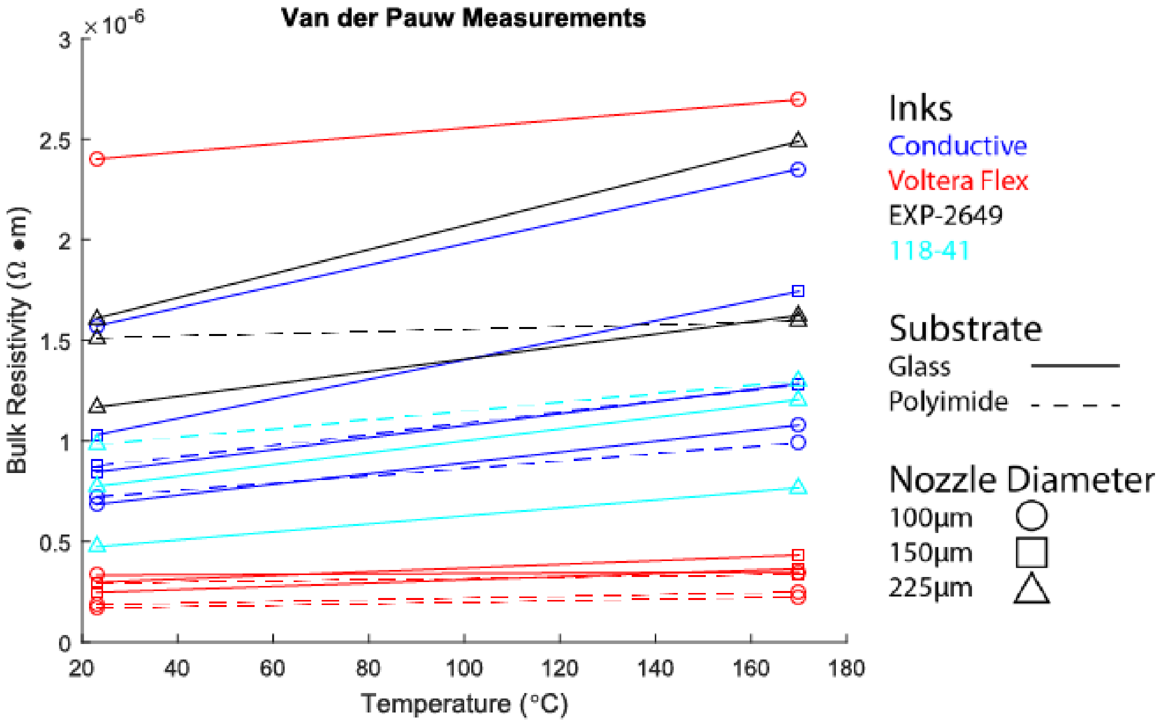


Figure 12: Bulk resistivity of specimens as a function of temperature.

Sheet resistance measurements for all of our specimens is shown in Figure 11. The results show that sheet resistance increases as temperature increases, which is expected and agrees with our RTD resistance measurements in Section 3. Also, the reference sheet resistance for the Voltera conductive ink (as provided by Voltera) is 0.012 Ω/□, which generally agrees with our results. It should be noted that there is no discernable pattern from just looking at the sheet resistance measurements, because they depend on the thickness of our specimens (which was not well controlled, as mentioned in section 4.3).

The resistivities of all of our specimens are plotted in Figure 12. Unlike sheet resistance, this measurement is independent of thickness. It can be seen from Figure 12 that the resistivity is highly dependent on the ink used, which is expected. The Voltera Flex ink had the lowest bulk resistivity while the EXP-2649 ink had the highest. The average resistivities of each ink are summarized in Table 1.

Table 1: Bulk resistivities of various inks.

Ink	Resistivity (Ω·cm) at 23°C	Resistivity (Ω·cm) at 170°C
Voltera Conductive	9.544E-5	1.455E-4
Voltera Flex	5.606E-5	6.643E-5
Creative Materials EXP-2649	1.429E-4	1.903E-4
Creative Materials 118-41	7.425E-5	1.090E-4
Pure copper (reference)	1.724E-6	2.833E-6
Pure silver (reference)	1.59E-6	3.02E-6

It should be noted that the reference resistivity for Voltera Conductive ink (provided by Voltera) is 9.5E-7 Ω·m, which matches our results. It should also be noted that the bulk resistivity of all of the inks is over an order of magnitude higher than that of pure silver. This should be expected, as the inks are composed of suspended silver particles. This is expected to have higher resistivity than a pure, continuous chunk of silver. Because of this, any wires printed using the Voltera should be considered “resistive” and wire resistances should not be neglected in critical applications. However, these inks are excellent for creating resistive elements (such as resistors, RTD sensors, and strain sensors).

5. Printing Challenges

5.1 Line Width

The width of a printed line is not only dependent on the choice of nozzle diameter, but also on the interactive relationship between the ink and substrate. Specifically, it is the wetting of the ink on a substrate that affects how much a deposited line will spread on the substrate surface. This is illustrated in Figure 13.

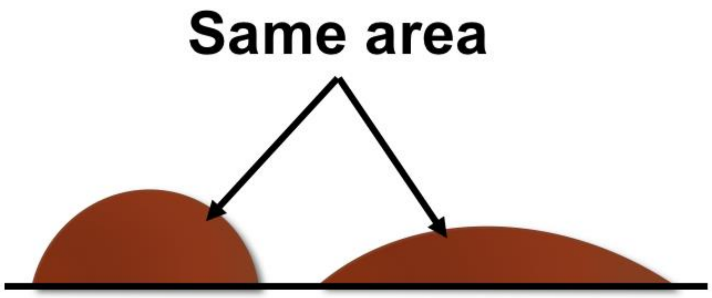


Figure 13: The ink on the left has a higher contact angle (less wettability) than the ink on the right (greater wettability).

Because the wetting properties are highly dependent on a particular ink-substrate combination, printing tests should be done to determine how much spreading will occur. This information is required to determine the minimum line width, and therefore the minimum spacing required between adjacent lines.

In our experiments, we measured the width of our printed RTDs under an optical microscope using a microscope calibration slide, as shown in Figure 14. The width normalized by nozzle diameter is given in Table 2 for various ink-substrate combinations.

Table 2: Normalized Line Widths for Various Ink-Substrate Combinations

	Substrate	
Ink	Glass	Polyimide
Voltera Conductive	2.058	2.792
Voltera Flex	2.158	3.678
Creative Materials EXP-2649	1.033	1.267
Creative Materials 118-41	1.000	0.911

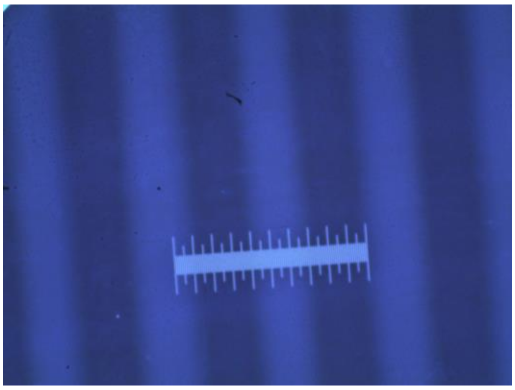


Figure 14: Optical microscope image of printed lines (dark regions) along with a calibration scale (1 mm full scale length).

5.2 Trim length & Thinning

The Voltera dispenses inks using discrete “kicks” with the dispensing plunger rather than by continuous extrusion (like most 3D printers based on fused filament fabrication). At the start of the kick, the ink flow rate is higher due to the larger backpressure inside the ink cartridge. As the backpressure dissipates, the flow rate reduces. This yields a smooth, even line that gradually thins out. The parameters that control the kick are the rheological setpoint (how strong the kick is), the trim length (the distance between kicks), and the anti-stringing distance (the amount of retracing the Voltera does between line segments to prevent open circuits caused by the kick).

Since the Voltera gives the ink cartridge periodic discrete kicks rather than continuous plunger depression, it must pause and re-kick the ink after the parameter “trim length” is reached. Until the ink is kicked, the trace gradually thins out as the circuit is printed. When it does re-kick the ink, it also re-traces the last trim by a parameter called the “anti-string length”, to prevent discontinuities.

The re-trace can be problematic for circuits with very tight spacing. As seen in Figure 15(a), the re-trace causes blobbing and short circuits. However, by properly adjusting the geometry and trim length such that the blob only appears in predictable and allowable locations, such issues can be minimized. This is shown in Figure 15(b) on the right, where the trim length was chosen such that all the blobs periodically appear on the bottom of the RTD and don’t cause short circuits.

Anti-stringing distance **Trim length**

(retrace distance per trim) (max distance in one path)

(a) (b)

Figure 15: (a) RTD with blobs and (b) Trim length correctly tuned.

6 Acknowledgements

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References

[1] Salowitz, Nathan, et al. "Integration and Deployment of Thick Film Piezoelectric Actuators/Sensors on Organic Stretchable Substrates", PhD Thesis, Stanford University.

[2] Guo, Zhiqiang, et al. "Functionalization of stretchable networks with sensors and switches for composite materials." Structural Health Monitoring (2017): 1475921717709632.

[3] Xu, Yuanyuan, et al. "The Boom in 3D-Printed Sensor Technology." Sensors 17.5 (2017): 1166.

[4] Van der Pauw, Leo J. “A Method of Measuring Specific Resistivity and Hall Effect of of Discs of Arbitrary Shape,” Philips Research Reports (1958)