

Inkjet Printing of Nano-Silver Conductive Ink on PET Substrate

A Senior Project

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By

Skyler Jiang

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Abstract

Printing of conductive ink traditionally uses copper-based ink and was used on high temperature metal substrates due to the high curing and sintering temperature of copper. In this experiment, however, Metalon JS-B25P nano-silver conductive ink was printed using an Epson Stylus C88+ inkjet printer on polyethylene terephthalate (PET) based Novele printing media made for low temperature applications. With silver's lower sintering temperature, the nano-silver particles in this ink are desired to be able to sinter at a low enough temperature to be used on the PET substrate. The printed ink traces were cured with a temperature-controlled hotplate at 100°C, 120°C, 140°C, and 160°C for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. The resistivity of these silver ink traces were calculated and compared to the bulk silver resistivity of $1.67 \times 10^{-8} \Omega\text{m}$ to $1.81 \times 10^{-8} \Omega\text{m}^1$, where the ideal resistivity of the silver ink traces would be less than 5 times that of bulk silver. A profilometer was used to measure the thickness of the thin ink film in order to calculate the resistivity. The ideal resistivities were not met, and the resistivity of the sample ink traces ranged from five to ten times the bulk resistivity. No significant statistical difference were observed across the different curing condition groups.

KEYWORDS

Nano-silver conductive ink, PET substrate, sintering, resistivity, bulk resistivity, profilometer

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1. Introduction

1.1 Conductive Ink Printing

Printed electronics is a technology that has been improving throughout this decade. This technology is used to create electrical devices on different substrates, such as making thin film transistors, capacitors, resistors, batteries, circuits, etc. There are many different methods of printing electronics, including screen printing, lithography, rotogravure, and screen printing. Although these methods are already low cost processes by electronic industry standard, a newer alternative, inkjet printing, can be even cheaper, more convenient, ease of mass production, sustainable, and grants flexibility.²

One of the most used methods in electronics printing is lithography. It is widely adopted in the circuit board industry for manufacturing circuits. This method involves many steps including etching, electroplating, etc. It can be extremely time consuming, and somewhat expensive. The etching agent used in lithography is also corrosive, and the choice of substrate is limited. Because of these downfalls, the electronics industry is seeking improvements from inkjet printing^{3,4,5}.

Inkjet printing requires low viscosity liquid-phase materials to be printed through a nozzle. The printed conductive ink will form a conductive line after drying. Inkjet printing's ability to deliver precise, small amount of ink in a quick fashion will make printing conductive ink easy, fast, and effective. Ideally, the printed ink will dry quickly after printed due to the inkjet's ability to keep the amount of ink small and precise. The conductive inks used for printing are typically made of copper and/or silver nanoparticles due to their high electrical conductivity in some kind of organic solvent and polymer coating^{3,4,5}.

1.2 Sintering

In order to reduce the ink into its corresponding metals, a sintering step is needed. Sintering is the material atomic diffusion process driven by the reduction in the interfacial energy between the metal particles. There are four possible diffusion paths during the sintering between two particles (Figure 1). Paths 1 and 2 do not cause densification while paths 3 and 4 do. Densification only occurs when the distance between the centers of the particles change⁶.

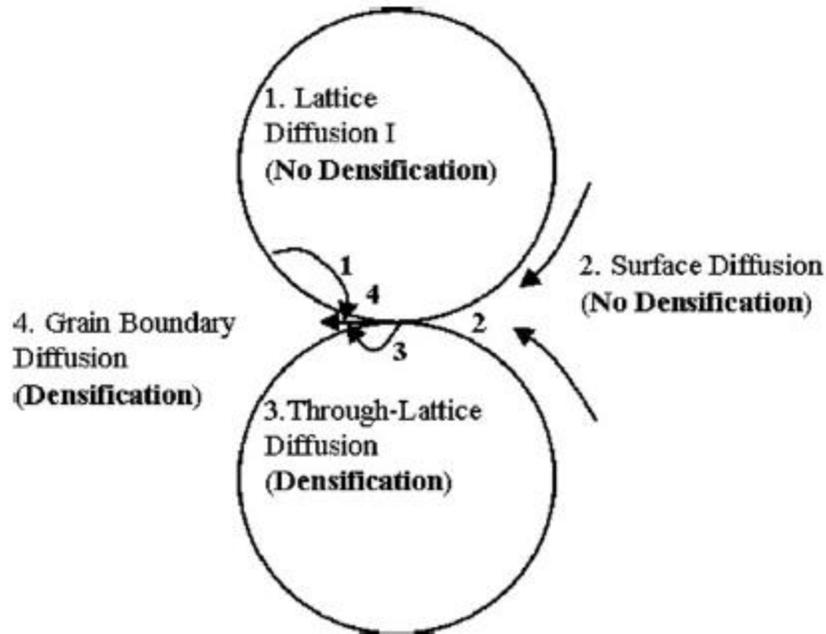


Figure 1. Possible diffusion paths between two metal particles during sintering⁶.

The sintering process can be low temperature due to the high surface to volume ratio of the nanoparticles. There are two different sintering techniques available. The conventional radiation-conduction-convection heating is the most commonly used method. The sintering temperatures for this process are usually above 200 degrees Celsius, making a selective number of substrates unusable such as thermoplastic polymers and paper. The other technique used is a laser sintering method. The laser follows and sinters the printed tracks, not affecting the substrate. It is much more effective compared to the previous technique. However, the laser method is usually very costly^{4,6}.

Without curing the printed ink trace and sintering the metal particles, nano-silver conductive ink acts as an insulator in its as-dried state⁶. The nano-silver particles are coated in a stabilizing polymer coating and submerged in a solvent designed to help initiate sintering at lower temperatures (Figure 2). At elevated temperature, the solvent would evaporate and the polymer coating would melt and flow away from the interparticle regions, forming an adhesive layer in between the ink and the substrate. This allows the metal particles to come in contact and sinter. Sintering not only renders the printed ink tracks conductive, it also affects the physical and electrical properties of the metal nanoparticle tracks. One major property that is linked to sintering is resistivity. With lower sintering temperatures, the resistivity of printed metal nanoparticle tracks can be up to 2 to 3 times lower than its theoretical bulk resistivity.

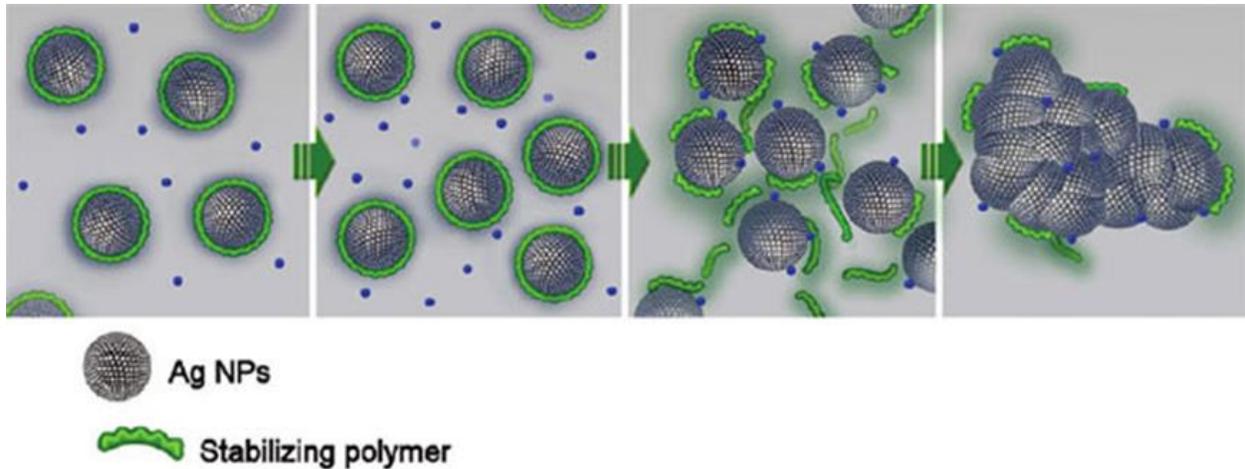


Figure 2. The movement of the nano-silver particles and the polymer coating at elevated temperatures during curing.⁷

1.3 Percolation Theory of Conductivity

The percolation theory of conductivity describes the statistical behavior of electrical conductivity in the clustered nano-silver particle system of the ink. When electricity travels through this cluster of nano-silver particle structure, the electricity has a probability to percolate from one particle to the next. This probability is depended on the density of the sintering of silver particles in the structure, where the probability of percolation is extremely low until a specific percentage is met. This percentage is called the percolation threshold. The percolation threshold can be determined experimentally for different systems. In order to obtain good conductivity in the ink traces, high degree of sintering is essential^{8,9}.

2. Experimental Procedure

2.1 Material

The ink used in this project was the Metalon JS-B25P nano-silver ink purchased from Novacentrix. The average silver particle size in this ink is 75 nm in diameter. The particles are coated with ethylene glycol and submerged in polyethylene glycol 4 (tert- octylphenyl) ether. The inkjet printer used in this project was an Epson C88+ Stylus photo printer purchased from Novacentrix. The substrate used in this project was the Novele printing media purchased from Novacentrix. The Novele printing media is a PET-based, transparent, mesoporous printing media made for conductive ink inkjet printing.

2.2 Sample Preparation

Sample traces were printed on 3.5 inches by 5 inches sheets of Novele PET film with three traces on each sheet as shown in Figure 3. After printing the sample traces, the samples were transferred to a hotplate to be cured. The curing conditions selected for this project were 100°C, 120°C, 140°C, and 160°C for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. With each sheet of three traces for each pair of temperature and time curing condition, a total of 16 PET sheets of samples were prepared (Figure 4). The resistances of each of the sample traces was measured after curing and recorded using a multimeter.

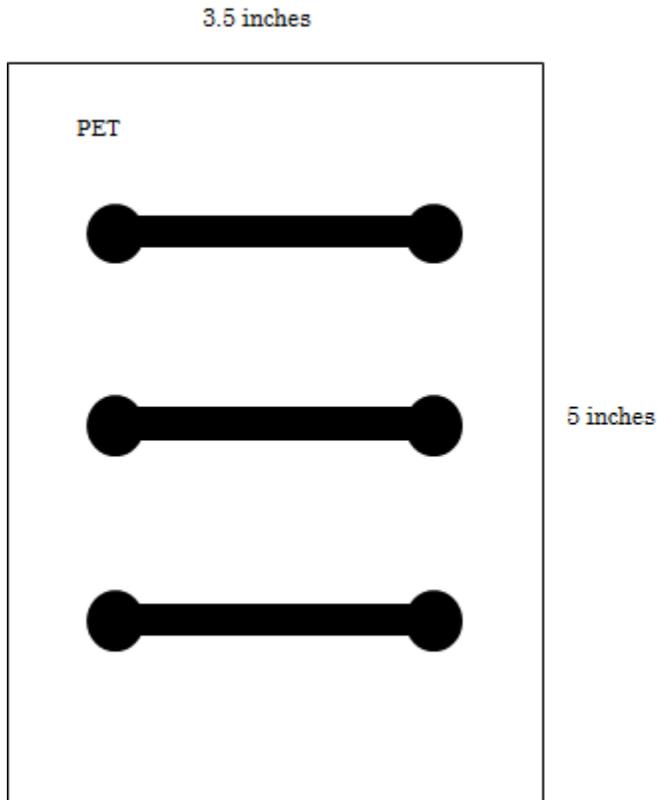


Figure 3. Diagram of the printed samples with three traces on each PET film.



Figure 4. 16 printed sample films with each sheet for one set of curing conditions.

2.3 Calculating Resistivity

The resistivity of the sample traces were calculated using equation 1¹⁰, where ρ is resistivity, R is resistance obtained from the multimeter, L is the length of the sample trace from end to end, and A is the cross-sectional area of the ink.

$$\rho = \frac{RA}{L} \quad (1)$$

Two different models were used to calculate the cross-sectional area of the ink trace. The first model used is shown in Figure 5, where the cross-sectional areas of the ink traces were assumed to be perfectly rectangular. With this model, the cross-sectional areas of each of the sample traces were calculated by multiplying the width of the traces by the thickness of the traces obtained using an AMBIOS Technology (XP-1) profilometer provided by the Cal Poly clean room. The profilometer measures the thicknesses of the ink films by dragging a needle across the surface of the samples and recording the vertical displacements of the needle tip, generating an array of data points. Due to the rectangular cross-section assumption of the first model, the thickness value was obtained by averaging the data point values from where the ink trace begins and ends on the profilometer graph (Figure 6).

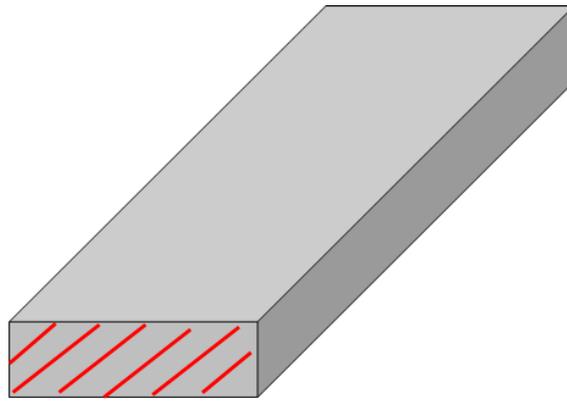


Figure 5. The assumed cross-section of the printed ink traces.



Figure 6. Example of a profilometer graph generated. For the first model, the thicknesses for the ink traces were calculated by averaging the data points from where the ink trace begins and ends, represented by the two red lines.

The second model used to calculate the cross-sectional area of the ink traces is more precise than the first model. In this model, the exact cross-sectional area of each sample trace was obtained using the profilometer data by calculating the area under the curve as shown in Figure 7.

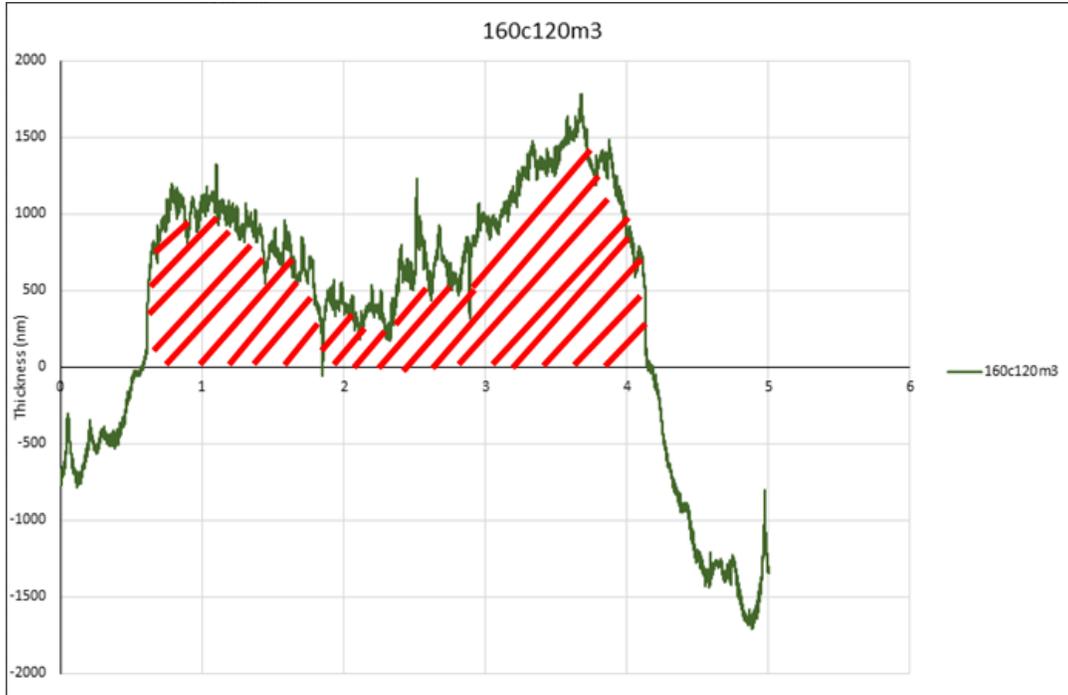


Figure 7. The second model used to calculate the cross-sectional area of the ink traces.

2.4 Light Microscopy

Light microscopy images were taken at 50x and 500x magnification using an Olympus BH2 UMA microscope provided by the Cal Poly Materials Engineering Department to observe the surface pattern of the ink traces.

3. Results

3.1 Model 1 Resistivity

Resistivity values calculated using the rectangular cross-sectional area model were plotted against the curing time for each of the curing temperature groups (Figure 8). As shown in the graph, none of the curing conditions met the desired resistivity of $9.05 \times 10^{-8} \Omega\text{m}$, which is five times the resistivity of bulk silver, represented by the red dotted line. To see if there are any significant statistical differences between the different sample groups, a 5% significance ANOVA test was performed. The ANOVA test yielded a P-value of 0.406, which is greater than

0.05, demonstrating that there is no significant statistical difference between the resistivity values of these curing conditions.

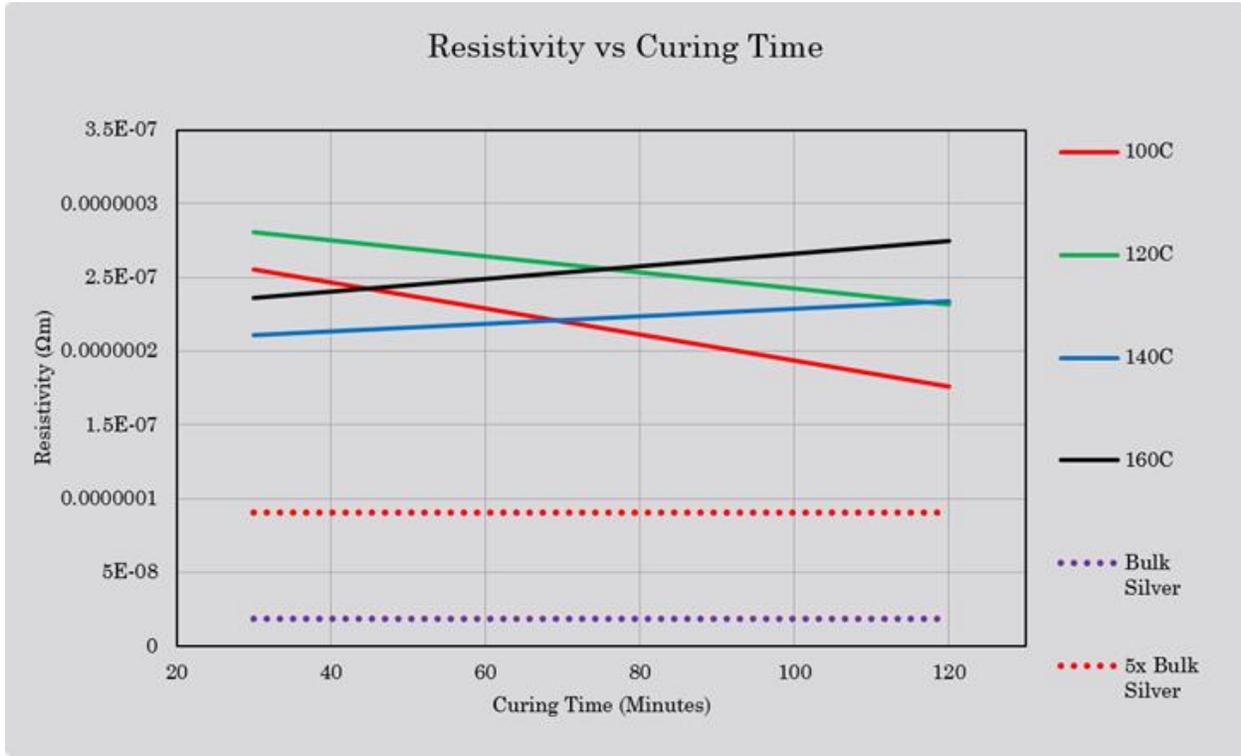


Figure 8. Resistivity from model 1 vs curing time.

3.2 Raw Resistance Data

Due to the lack of statistical difference in model 1 resistivity results, the raw resistance data were plotted against the curing times for each of the curing temperature groups (Figure 9). A 5% ANOVA test was performed, and it yielded a P-value of 0.012, which is less than 0.05, meaning that there are significant statistical differences between the temperature groups. By conducting a Tukey pairwise comparison test, differences were found to reside between the 100°C and the 160°C groups, and between the 120°C and the 160°C groups. Since the raw resistance data showed significant differences between some of the groups while the model 1 resistivity data did not, the thickness values used to calculate resistivity were speculated to be the source of the problem.

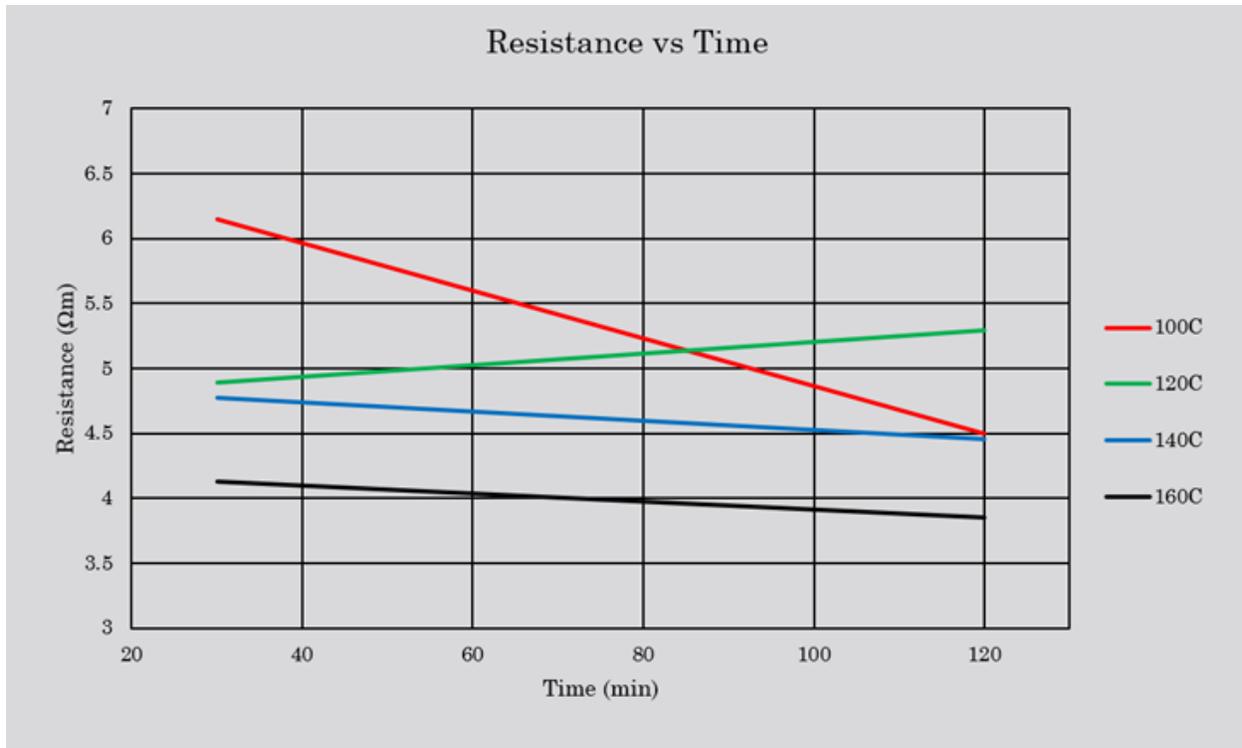


Figure 9. Raw resistance data vs curing time.

3.3 Light Microscopy Images

Since the thickness values were speculated to be inaccurate, the rectangular assumption of the cross-section area was questioned. For confirmation, light microscopy was performed on the sample ink traces to observe the ink film on a microscopic level. As shown in Figure 10C, since the ink traces were printed horizontally, the area between each printed trace has a thinner layer of ink. This showed that the cross-sectional area of the printed ink trace is not close to a rectangular shape, which might have contributed to the insignificance in the resistivity data.

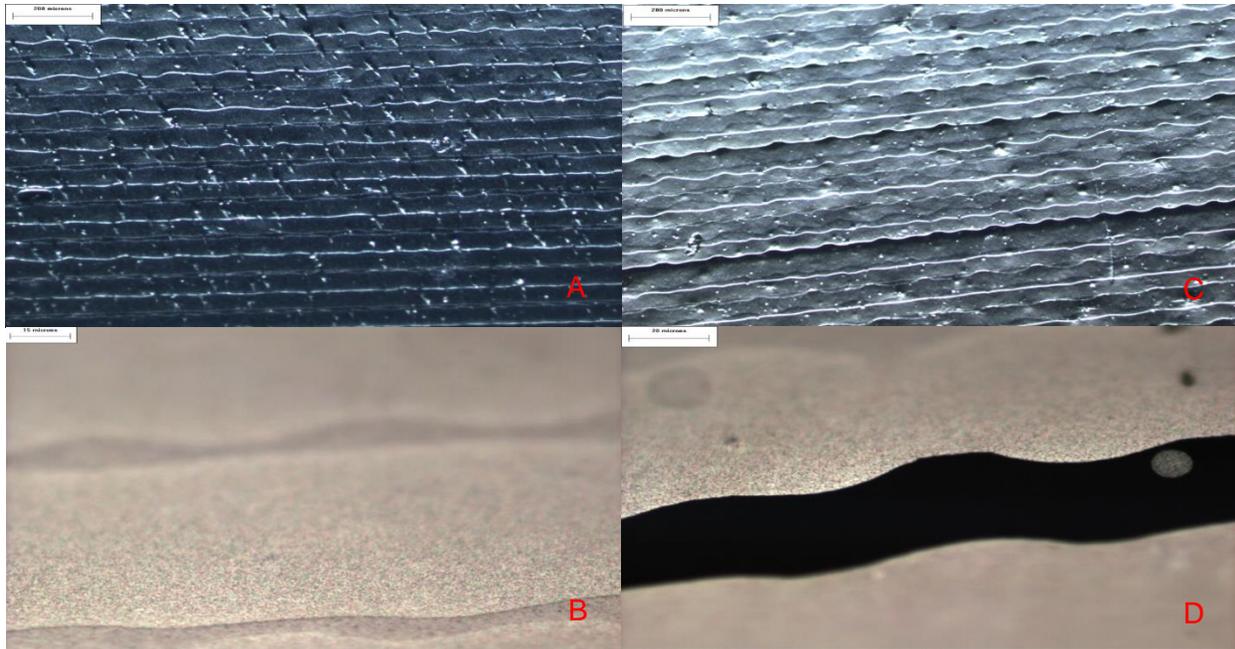


Figure 10. Light microscopy of 2 different sample traces cured at 140°C for 30 minutes: first sample at (A) 50x and (B) 500x, second sample at (C) 50x and (D) 500x.

3.4 Model 2 Resistivity

Resistivity values were calculated using the exact cross-sectional area model and were again plotted against the curing time for all the curing temperature groups (Figure 11). As shown in the graph, none of the curing conditions met the desired resistivity of $9.05 \times 10^{-8} \Omega\text{m}$, and with a 5% ANOVA test, the data yielded a P-value of 0.0983, showing no significant differences between the data groups.

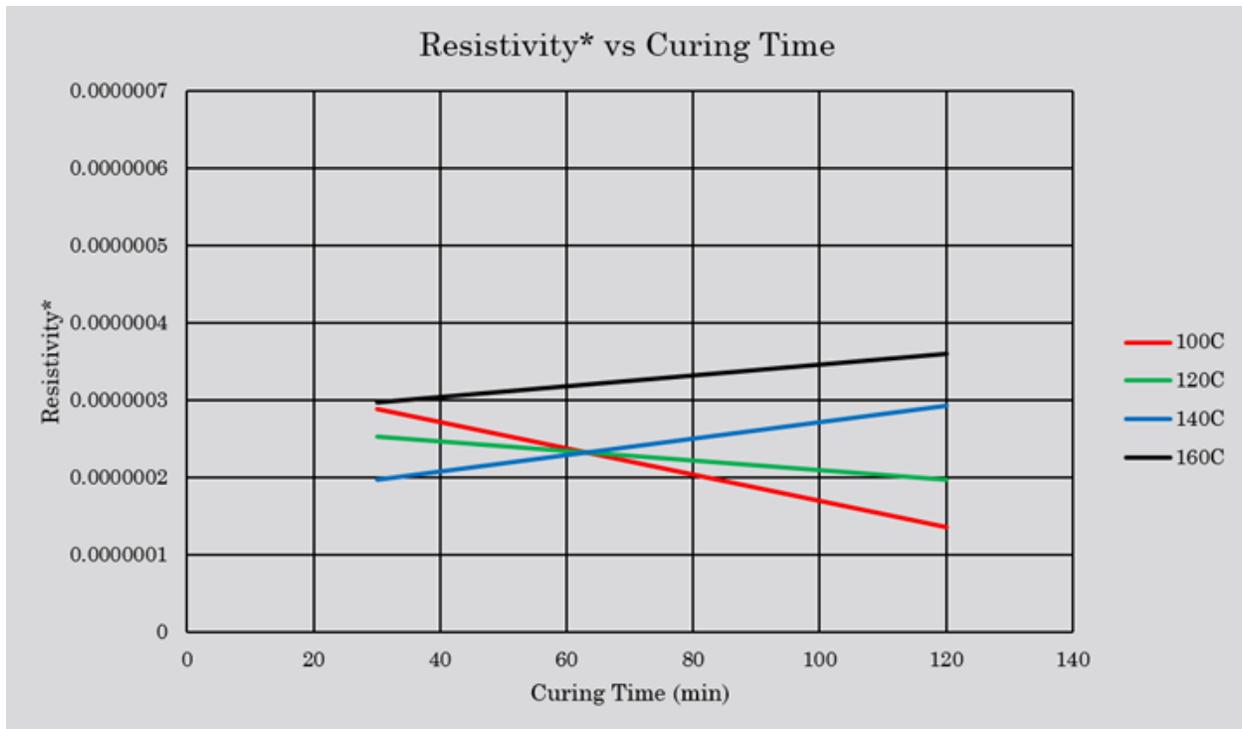


Figure 11. Model 2 Resistivity vs curing time graph.

4. Discussion

4.1 Resistivity

Both model 1 and 2 resistivity data did not meet the desired resistivity, and no significant differences were found between the data sets for both the models. Although the raw resistance data did show differences between some of the groups, those differences were not shown in the resistivity data. Overall, the resistivity of the sample ink traces ranged from $1.4 \times 10^{-7} \Omega\text{m}$ to $3.5 \times 10^{-7} \Omega\text{m}$. There are many factors that could have contributed to the yielding of the high resistivity values on the sample ink traces.

4.2 Possible Factors Contributing to High Resistivity

4.2.1 Sample Printing

Light microscopy results showed inconsistencies in the printing of the sample traces. Many gaps, holes, and other defects can be observed on the surface of the sample traces. For example, as shown in Figure 10C and Figure 10D, large, through sample gaps were found on that specific sample ink trace. Since the resistance values were measured using one point on each end of the

trace instead of measuring across the whole width of the sample (Figure 12), these defects could have yielded higher resistance values.



Figure 12. Measuring resistance using one point on each end (top) measuring across the width (bottom).

4.2.2 Curing Process

One of the initial milestones for this project is to build an Arduino-controlled insulated heating pad with precise temperature control (Figure 13). However, the apparatus broke down during one of the test runs due to overloading, so an uninsulated hot plate was used as a substitute for the curing of the samples due to time constraints. The uninsulated curing environment could have caused the curing temperatures to fluctuate and to be lower than expected.

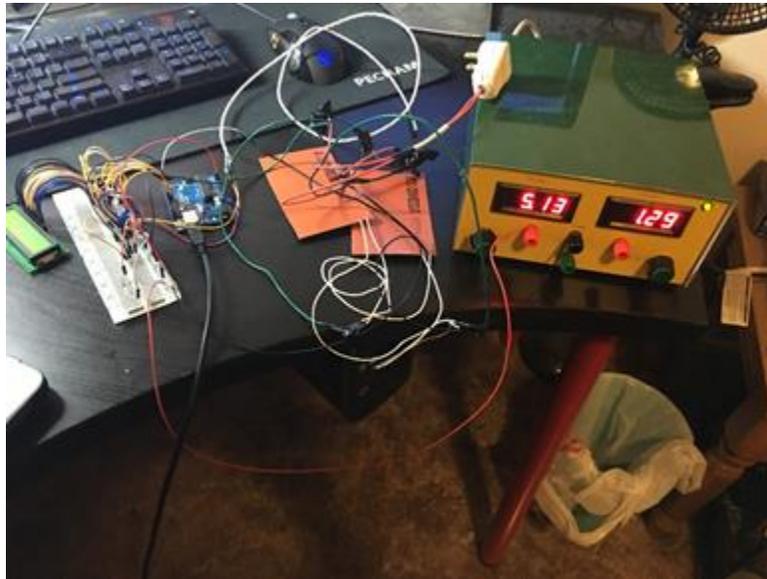


Figure 13. Arduino-controlled heating pad with precise temperature control built for the curing of the ink samples..

4.2.3 Profilometer

Another possible factor is the thickness data obtained using the profilometer. Many of the profilometer results were inconsistent and contain a lot of noise (Figure 14). The inconsistency

and noise could have been caused by the unevenness of the PET substrate. Since the resistivity values were heavily dependent on the cross-sectional area of the sample (Equation 1), the possible faulty profilometer reading could have altered the resistivity results.

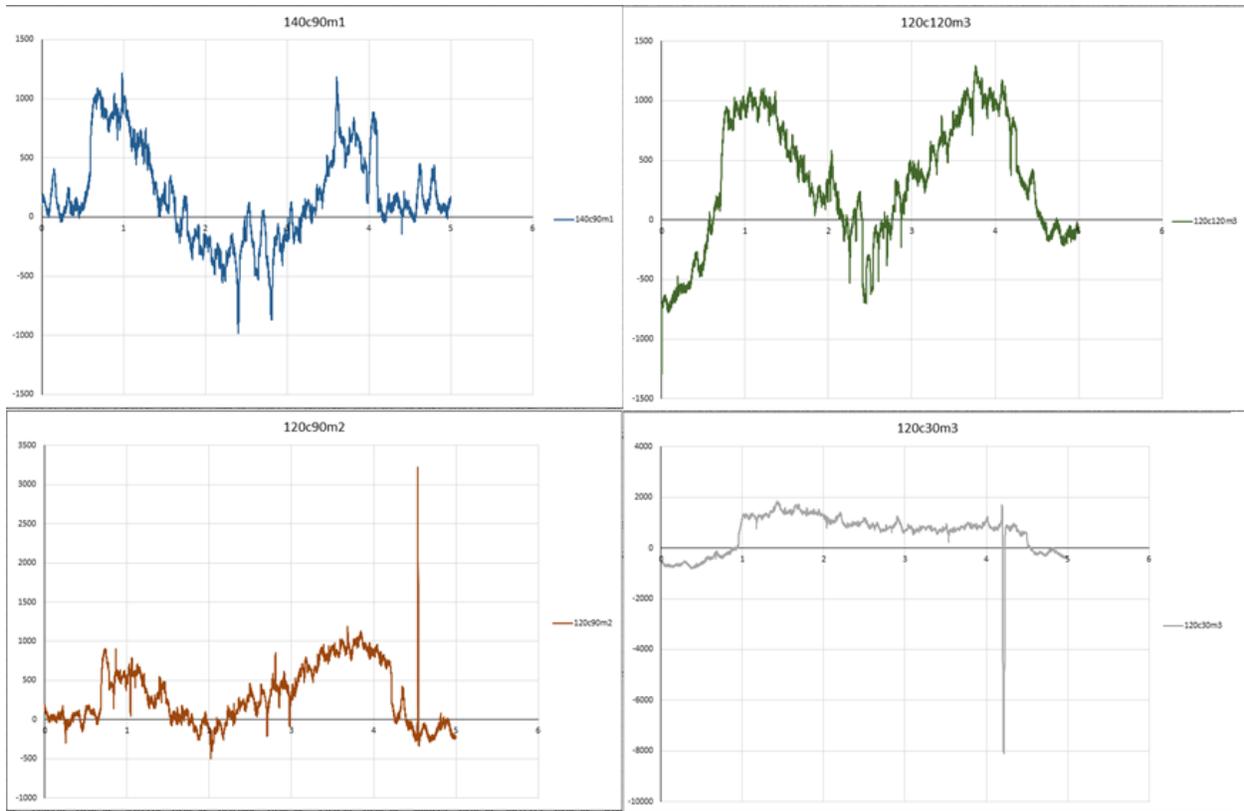


Figure 14. Examples of inconsistent profilometer results with noise.

5. Conclusion

1. None of the curing conditions yielded a desired resistivity of $9.05 \times 10^{-8} \Omega\text{m}$, 5 times that of bulk silver. The resistivity values ranged from $1.4 \times 10^{-7} \Omega\text{m}$ to $3.5 \times 10^{-7} \Omega\text{m}$.
2. The 100°C and 120°C groups had significantly higher resistance values than the 160°C group. Otherwise, there are no other significant differences across the different curing conditions.
3. More testing and study is needed to conclude and understand curing nano-silver ink at low temperatures.

6. Acknowledgments

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