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Characterization of Aerosol Jet Printed Silver Thin Films Sintered by a Scanning Laser

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CHARACTERIZATION OF AEROSOL JET PRINTED SILVER THIN FILMS SINTERED BY A SCANNING LASER

A Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

by

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B.S.M.S.E., The Ohio State University, 2019

2023
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ABSTRACT


Direct write printing, which is part of additive manufacturing (AM) technology, offers unique capabilities that can complement traditional methods of electronics fabrication. Printing of electrical interconnects via aerosolization is one of the areas in AM that is very important in electronics fabrication. Post-print sintering is a critical step in printed electrical interconnects because it strongly influences the electrical resistivity of the interconnects. Interconnects require the lowest possible resistivity to achieve better performance. Thermal sintering is the most common technique employed in printed interconnects. However, it is limited to substrates that can handle the high temperature requirement for sintering. For polymers or other substrates with low thermal budget such as the ones used in wearable electronics, sintering becomes a challenge. In this work, we explored a scanning laser technique as an alternative to thermal sintering. In this study three separate ink materials (two from ElectronInks, and one from Novacentrix) were considered. First, optimal printing parameters such as sheath pressure, atomization pressure, and atomization current for each ink material were identified. Next, characterization of printed silvers sintered by different laser power conditions was performed to determine optimal sintering conditions. This characterization includes quantifying DC resistivity, temperature coefficient of resistance, surface morphology and porosity. Results from this work demonstrate some advantages of
this sintering technique such as being able to selectively wash off un-sintered silver, which is attractive for fabricating strain sensors or other microelectronic applications.
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I. Introduction and Literature Review

1.1. Objective

Additive manufacturing is a rapidly growing [1] field of fabrication techniques that enable new ways to design and develop components of both simple and complex geometry. Materials utilized for additive manufacturing may initially have gaps in their abilities to perform in specific environments or specialized tasks. Exploring these deficiencies in material ability, new methodology can be employed to address these gaps in ability and create a new approach to an otherwise missing link.

This thesis explores the abilities of a novel silver ink formulation provided by ElectronInks to determine desirable electronic materials properties for employment in potential packaged electronics. Print parameters and their impact on aerosol jet printing were observed. Measurements of resistance in relation to sintering conditions to determine resistivity values were collected, as well as measurements of resistance in relation to operating temperature. These values are correlated to common desired electronic properties to address corrective actions to apply to materials under varied conditions. These investigations attempt to contribute new potential best practices to be utilized upon employment of silver printable inks.

1.2. Additive Manufacturing

Additive manufacturing is the construction of components layer by layer, instead of being cut, milled, or otherwise subtracted from to produce a completed part. More traditional manufacturing processes are sometimes referred to as “subtractive manufacturing” where components are created from similarly shaped bulk pieces of the desired material. These parts are then reduced by chipping, milling, cutting, or other forms of removal until the desired part is
left. The term additive manufacturing in some ways has become synonymous, though somewhat erroneously, with the broader term of three-dimensional printing. Outside the realm of engineering, consumer based three-dimensional printers can produce components layer by layer using a variety of materials ranging from plastics to resins using generated procedures from supporting software. Within the confines of engineering however, while the process of producing parts layer by layer is the same, the material utilized can vary from more consumer-based polymer materials of plastic or resins to more engineering focused materials such as metals or ceramics.

The process of additive manufacturing holds several key advantages over current traditional methods of manufacturing. The prime example being that the use of additive manufacturing enables very complex geometries to be developed that otherwise are impossible for subtractive processes to perform [2]. This enables components to be developed with less weight and less waste than traditional manufacturing as it is not necessary to procure more material than is needed for one component [3].

Additive manufacturing can utilize several different processes and material systems as stated. Some processes simply extrude heated material onto a build plate layer by layer, while others use ultraviolet light to cure resin layers on a build plate. Other processes include scanning a laser over a bed of powdered material to selectively melt desired shapes on each layer or utilizing aerosolized ink materials to jet onto a substrate to build thin layers. Each of these processes can be tailored to fit the needs of the component. Table 1 indicates different additive manufacturing processes.
Common commercial three-dimensional printers fall within either the extrusion or photopolymerization categories. In extrusion based additive manufacturing, a spool of polymer filament is fed through a heated print head. The heat from the print head allows the polymer to extrude onto the relatively cold build plate or layered polymer below. After cooling, the polymer can be removed from the build plate for a completed part.

In photopolymerization, liquid polymers or resins are poured into a build chamber or vat. A build plate is then lowered into the build chamber and selective patterns of ultraviolet light
cure the polymer into its desired shape. The build plate moves up to separate the build plate from the ultraviolet source, then returns the surface to the source and continues to the next layer where the process repeats itself and another layer is cured.

1.2. 1.3. Direct write printing

Direct write additive manufacturing involves the fabrication of functional components on a substrate without an intermediate fabrication step [6].

Direct writing methodology involves directly placing the desired shape onto a selected substrate without masks or stencils. Writing on a piece of paper compared to typing the same memo out on a computer and printing a copy serves as a real world non-engineering difference between direct write and other technologies. Figure 1 shows a generalized example of direct write printing.

![Image of direct write additive manufacturing](image)

*Figure 1: Example of direct write additive manufacturing [7]*
Fabrication of samples via direct writing technology can take various forms. Components can be fabricated via extrusion, like common commercial additive practices. Material is applied via an extruder onto the substrate to fabricate a functional component. Components can also be fabricated via jetting practices either through ink jet printing or aerosol jet printing, where a material is applied to the substrate in the form of droplets or an aerosol.

1.4. Aerosol Jet Printing

Aerosol jet printing is a direct write method of producing traces of different materials such as metals, dielectrics and polymers [8] on a selected substrate utilizing one of two primary delivery methods to jet aerosolized ink onto a surface.

Aerosol jet printing has two methods of producing aerosolized ink to direct towards a substrate. All aerosol jet printing is performed as either pneumatic atomization or ultrasonic atomization. Pneumatic atomization is performed using pneumatic pressure systems built into an aerosol jet printer to drive viable ink through the system. By creating pressure differentials, the loaded ink can create droplets that are accelerated towards the substrate. Pneumatic atomization is able to utilize larger print volumes of ink to create the necessary pressures for printing and is capable of using inks with viscosities of 1 – 1000cp. Ultrasonic atomization, on the other hand, utilizes ultrasonic vibration to agitate inks which are then pressurized through the system and delivered onto the substrate. By applying current to a built-in transducer in the ink assembly, standing waves within the ink are created. At the peaks of these waves, shear forces take over and sever droplets of ink away from the remaining volume. At this point, other pressures take over and the aerosolized droplets are directed towards the substrate for deposition. Ultrasonic atomization is capable of small print volumes, ranging around 2mL of a desired material with a
viscosity limit of 1-10cp. This thesis utilized ultrasonic atomization techniques to fabricate samples.

![Ultrasonic atomization setup](image)

**Figure 2: Ultrasonic atomization setup [9]**

The fabrication of samples for ultrasonic aerosol jet printing is controlled by three main attributes: sheath pressure, atomization pressure, and atomization current. Atomization current, as previously mentioned, is the current applied to the transducer to create standing waves in the ink and allow shear forces to take over. In the non-engineering world, this effect could be replicated by placing the head of a multi-power electric toothbrush in water. The vibrations of the brush head agitate the water, causing water droplets to rise. The higher the setting, the more water will be displaced. The same occurs with the transducer inside the ink assembly. Higher currents will create more aerosolized ink droplets. Atomization pressure refers to the pressure of the carrier gas inside the ink assembly measured in standard cubic centimeters per minute (SCCM) it is equivalent to 1cm³ STP/min. STP refers to standard temperature and pressure which is defined as room temperature (~25°C) at sea level (1 atmosphere). The carrier gas inside
the ink assembly carries the aerosolized droplets from the ink vial to the print head. Sheath pressure refers to a focusing gas inside the print head that collimates the aerosolized ink into a desirable jet while simultaneously ensuring the ink does not collect on the inside of the print head, causing a clog. If the sheath pressure is too low, the ink will begin to collect on the inside of the print nozzle, causing jetting to appear wet. Likewise, if the pressure is too high, the ink will not have enough time to collect with other particles, resulting in a “dry” print with droplets scattered on the substrate. Figure 3 shows the before and after results of each state of printing.

![Figure 3: Ink states relative to AJP](image)

All three of these pressures come together to create an aerosolized ink at steady state to produce usable traces.

1.4. Ink Systems

There are two primary ink types utilized for aerosol jet printing. These are either particle based inks or particle free inks. Particle based inks are inks containing metal nanoparticles that
when subjected to heat, light, or plasma, bond the metal particles together to create a conductive path. Particle free inks are instead made up of a metal – salt chemical complex. When the complex is subjected to heat, light, or plasma, the salt of the complex undergoes a chemical reaction, leaving behind the metal. The focus of this study includes two particle free inks formulated by ElectronInks, designated EI-615 and EI-616, and one particle-based ink formulated by Novacentrix, designated JS-A221AE. All the inks included in this study are silver based.

Silver was selected as the primary material due to its extremely desirable electronic properties as a noble metal. Compared to the other noble metals, silver has the highest conductivity/lowest resistivity of the noble metals while still retaining a low cost.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Material Conditioning</th>
<th>Resistivity at 20°C (μΩ·cm)</th>
<th>Conductivity at 20°C (S/m) x10^6</th>
<th>Cost (USD/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>annealed</td>
<td>1.6</td>
<td>62.9</td>
<td>0.76</td>
</tr>
<tr>
<td>Copper</td>
<td>annealed</td>
<td>1.7</td>
<td>58</td>
<td>0.0084</td>
</tr>
<tr>
<td>Gold</td>
<td>annealed</td>
<td>2.2</td>
<td>45.5</td>
<td>1943.19</td>
</tr>
<tr>
<td>Platinum</td>
<td>annealed</td>
<td>10.5</td>
<td>9.5</td>
<td>31.99</td>
</tr>
</tbody>
</table>

Table 2: Comparison of the noble metals [10]

1.5. Sintering

Sintering, by materials standards, is the heating of a coarse powder or droplet-based material in an “green” or pre-treated state into a solid or porous mass under the melting temperature without liquefaction [11, 12]. Current standard practices of aerosol jet printing utilize thermal sintering methods to evaporate or burn off nonmetallic particles in ink. The remaining material after sintering is a desired conductive trace that can be incorporated into integrated circuits. Samples treated with thermal sintering methodology are evenly sintered across the substrate, however the process is not selective and results in the entirety of the sample
being treated at the same time. Samples created via aerosol jet contain overspray particles.

Overspray, shown in figure 4, is additional material jetted onto a substrate that does not conform to the design parameters as a result of the column of aerosolized material spreading out in a cone like shape after leaving the print head.

![Figure 4: Example of overspray of a thermally sintered aerosol jet printed conductive silver trace [13]](image)

These isolated particles are thermally sintered in place, and if present in large enough density, create shorts in printed integrated circuits. To account for this and improve overall resolution of printing, laser sintering can be carried out. By selectively heating certain areas of ink with a laser, intricate patterns and traces can be created [14]. By performing post-processing on laser sintered samples, all non-sintered material can be removed. Laser sintering, and subsequent additional post-processing steps to remove non-sintered depositions, allows for the removal of overspray while retaining the accuracy of the print path that is not possible with thermal sintering methods [15]. This method of printing results in samples with a higher resistivity when compared to thermal samples, however the improvement of resolution and removal of overspray serves as a worthwhile tradeoff. Figure 5 shows the achieved resolution of performing laser sintering on printed silver.
1.6. Hybrid Manufacturing

As discussed, additive manufacturing is the creation of components layer by layer, an opposition to creating components from traditional manufacturing means. However, the combination of both additive and subtractive manufacturing, known as hybrid manufacturing, is also continuing to grow. Certain post-processing steps of three-dimensional printing call for the clean-up of printed components, or the removal of support materials. These subtractive processes can be referred to as hybrid manufacturing as both modern and traditional means are employed.

1.7. 2.5 Dimension Printing

The purpose of this study is to develop and characterize a novel ink’s printing parameters for the successful creation of electronic devices. Electronic devices are micro – nano scale creations that do not require large assemblies commonly seen in traditional three-dimensional printing. The prints performed in this study classify as 2.5 dimensional prints, while they
physically exist in three dimensions, their features and properties act according to two
dimensional calculations and concepts.

1.8. Electrical Measurements

This work performed two distinct sets of electronic measurements to assist in the
characterization of the studied provided ink formulas. These two sets include analyzation of
resistivity, and calculation of thermal coefficient of resistance. These two measurements apply
directly to the intended application of the chosen inks.

Resistivity ($\rho$) is a material property, measured in Ohm-meters ($\Omega \cdot \text{m}$) that is indicative of
its innate ability to resist the flow of electrical charges. It is the conjugate value to conductivity
which is indicative of a material’s ability to conduct electrical charges [16]. This is directly
related to a specific materials band gap width. The band gap is the distance between energy
layers of valence electrons in the valence band, and the energy layers of the conduction band.
Figure 6 shows the variance in band gaps between three common material classes.

![Figure 6: Relative band gap comparison of three classes of materials [17]](image)

Insulators are materials with extremely large band gaps. To conduct electricity in an
insulator, large amounts of energy need to be added to the system to move electrons to the
conduction band if the material itself does not begin to deteriorate before this is achieved [18].
Insulators have very large resistivities on the range of $1 \times 10^8$ to $1 \times 10^{16} \ \Omega \cdot m$. Common examples of insulators include wood, rubber, and glass.

Semiconductors are materials with smaller band gaps that can readily be made conductive with the addition of energy to the system in question [18]. Semiconductors have an extensive range of uses from common light emitting diodes (LEDs) to complex circuitry found in common electronics. Semiconductors have lower resistivities compared to insulators, on the range of $1 \times 10^{-5}$ to $1 \times 10^3 \ \Omega \cdot m$. Semiconductors include materials such as silicon, germanium, and carbon.

Conductors are materials in which the valence band and conduction band overlap. These materials, often either metals or metal alloys, readily allow the flow of electricity without the requirement of additional energy to the system [19]. Conductors have very small resistivities on the order of $1 \times 10^{-8}$ to $1 \times 10^{-5} \ \Omega \cdot m$. Common conductors are copper, silver, gold, and platinum of the noble metals, along with varied metal alloys.

The measurement of resistivity is performed in one of two methods. These methods are dependent on the physical size of the component or sample being measured. However, both methods employ a four-point probe setup to acquire electrical data. A four-point probe is an electrical contact that runs current and voltage simultaneously through a straight line, separated by a uniform distance as seen in Figure 7.
Figure 7: Four-point probe generic setup, probe distance S and sample thickness T [20,21]

This setup employs the ideas found in Ohm’s law to derive an equation that calculates the resistivity by way of a measured resistance shown in equations 1 - 10 [20].

\[ V = I \cdot R \quad (1) \]

\[ \rho = \frac{1}{\sigma} \quad (2) \]

Equation 1 is the common definition of Ohm’s law stating that voltage (V) is equivalent to current (I) multiplied by resistance (R). Equation 2 is the definition of resistivity being the inverse of conductivity.

\[ J = \sigma \cdot E = \frac{E}{\rho} \quad (3) \]

Equation 3 is the scalar form of Ohm’s law with current density (J) and electric field (E).

\[ E \equiv -d\phi/dr \quad (4) \]

Equation 4 defines the electric field as the negative partial derivative in electric potential (\( \phi \)) over the change in coordinates in the direction of current flow.
\[ d\phi = -\rho \cdot J \cdot dr \quad (5) \]

Equation 5 is the combination of equations 3 and 4, showing the partial derivative of electric potential equivalent to the negative resistivity multiplied by current density and partial derivative of current flow.

\[ J = \frac{I}{A} \quad (6) \]

Equation 6 is the general form of current density under the assumption of a uniform cross section.

\[ V = \rho \cdot I \cdot \frac{L}{A} \quad (7) \]

Equation 7 is the result of the integral over the length of the resistor (L)

\[ J = \frac{I}{\pi r^2} \quad (8) \]

Equation 8 shows the assumption of spherical coordinates in reference to the point of contact on a substrate.

\[ V = \left(\frac{\rho l}{2\pi}\right) \left[\frac{1}{S} - \frac{1}{(2S)}\right], \quad r = 2S \quad (9) \]

Equation 9 is the result of assumptions of current flow flowing outward through the probes at a distance of S from one another.

\[ \rho = 2\pi S \cdot R \quad (10) \]

Equation 10 is the total result of resistance spreading throughout the probes, indicating resistivity equating to \(2\pi S\) multiplied by the measured resistance over the probes.

This setup and calculation is applicable for large samples, where the thickness of the sample is greater than the separation of the probes (\(T >> S\)). However, when the thickness of the sample becomes too small, or much smaller than the probe separation distance, the equation changes to Equation 11.
\[ \rho = \left( \frac{\pi T}{\ln(2)} \right) \cdot R \quad (11) \]

Equation 11 shows the resistivity of a thin conductive sample equal to the thickness (T) of the sample multiplied by pi over the natural log of 2, multiplied by the measured resistance over the probe configuration. The setup is identical to a thick conductor sample, as seen in figure 8.

![Four-point probe setup for thin conductive pads, [20,21]](image)

In both equations, a resistance measurement is taken as indicated in R, and subsequently multiplied by the cross-sectional area in a thick conductor, or the thickness of the thin conductor to calculate the resistivity of the sample.

1.9. Temperature coefficient of resistance

A common trend seen in metals, and other conductive media, is that as temperature increases, measured resistance increases as well [22]. The sensitivity of a material’s resistance with temperature, or simply, how much the resistance changes at a given temperature, is known as the temperature coefficient of resistance (TCR) and is denoted by the Greek letter \( \alpha \) with units denoted \( 1/°C \). Equation 12 shows the relationship between temperature and resistance, incorporating the \( \alpha \) value [23].
\[ R = R_0[1 + \alpha(T - T_0)] \] (12)

To measure a material’s temperature coefficient of resistance, it is connected to a four-point probe setup identical to a resistivity measurement setup, as well as a thermometer. An initial temperature and resistance measurement is taken, denoted \( T_0 \) and \( R_0 \) for temperature and resistance respectively. Temperature is then increased incrementally, and resistance measurements are taken at each increment. A similar set of measurements is then taken as the sample is cooling. Collected data points can then be plotted and trend lines fit to the data to determine the slope of the data. This slope shows how the resistance will change with temperature and is the \( \alpha \) value. Temperature coefficient of resistance values for common materials are shown in table 3.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha ) (1/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>0.003819</td>
</tr>
<tr>
<td>Copper</td>
<td>0.004041</td>
</tr>
<tr>
<td>Gold</td>
<td>0.003715</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.003729</td>
</tr>
<tr>
<td>Iron</td>
<td>0.005671</td>
</tr>
</tbody>
</table>

*Table 3: TCR values for noble and common metals [24]*

1.10. Microscopy

Microscopy involves the use of microscopes to view and analyze physical details of a given sample. The type of microscope utilized can help determine what branch of microscopy it falls under, as well as its uses and limitations. Characterization of samples requires a thorough understanding of both features that are measured, but not physically seen such as resistivity, or thermal coefficient, as well as features that are physically seen such as a samples microstructure.
With optical microscopy, light is passed either onto or through the sample in a uniform manner over a field of view [25] to generate an image through an eyepiece that a user is able to physically look through, or with digital optical microscopes, is able to see through a screen. Optical microscopy is a straightforward and extremely cheap method of characterization. Users do not need a large amount of training, if any at all, to operate lab table microscopes and the environment in which an optical microscope is placed is much more dynamic than other forms of microscopy. These benefits are not without drawbacks, as optical microscopes are limited to relatively low magnification values of less than 2000x [26]. Images taken with optical light microscopes are limited in appearance to two dimensional cross sections, which while useful for specific applications, is a limiting factor for most others. Images taken with optical light microscopes must also be reflective or transparent enough depending on the microscope to ensure an image can be generated for the user to see. Optical microscopy is still widely utilized today as an “initial pass” of characterization to determine areas of interest to explore using other methods of microscopy.

In 2012, Zhao et al. utilized optical microscopy to characterize failure modes of aerosol jet printed strain sensors [27]. The work explored the potential of additive fabrication of electrical components and methodologies to characterize and compare to commercially available, non-additively fabricated devices.

In 2019, Serpelloni et al. utilized optical microscopy to determine substrate penetration of silver-based aerosol jet printed traces for the creation of printed smart devices [28]. The work performed electrical analysis on fabricated devices, utilizing optical microscopy to determine print quality for printed components.
In 2022, Yoo et al. utilized a Keyence VK-x1000 Optical microscope on aerosol jet printed conductive traces [29] to study morphology. The work attempted to find a “benchmark” for additively printed trace optimization studies.

In 2023, McKibben et al. performed optical microscopy on silver-based aerosol printed components to profile print quality and provide data for electrical calculations [30]. The work concluded the ability to produce electronic components using additive methodology to address current issues in component fabrication.

Scanning Electron Microscopy (SEM) utilizes a focused electron beam column scanning over a solid, non-powdered sample to generate an image representing the surface of interest [31]. The scanning of the electron column over the substrate bombards the sample, reflecting incident electrons at specific angles. Incident electrons are captured by detectors inside the microscope chamber to produce an image for capture and analysis. Scanning electron microscopy is a more in-depth method of characterization, requiring users to have a moderate amount of training to properly operate any microscope. The level of required training is dependent on individual microscopes and the number of additional tools that are built in. Images captured with scanning electron microscopy can produce high magnification images on the order of 60 – 100,000x magnification depending on the microscope. Scanning electron microscopes, however, are expensive to obtain, and as such most microscopes are shared between research teams to reduce costs. This has the added drawback of availability depending on the research team population. Large institutions may have to reserve timeslots weeks or months in advance for users to be able to collect images, whereas smaller groups might be able to get by with availability within a few days. Scanning electron microscopes also require very controlled environments to be able to
produce quality images. Vibrations from any source can potentially be detrimental to the collection of images.

Energy-dispersive X-ray spectroscopy (EDS) is an available add on to an electron microscope that can perform elemental analysis on a sample to determine the constituent elements that compose it. Electrons generated inside the microscope can excite valence electrons in the sample, causing them to enter a higher energy state. To return to ground state, these electrons emit a photon of light in the form of an X-ray which has a quantized amount of energy unique to elements, acting as a fingerprint to each specific element. Detectors inside the microscope chamber measure the energy of each photon to determine which element it originated from [32]. EDS is a valuable tool, acting as a sanity check for substrates to determine factors that could play into skewed data sets, or as a method of characterization by highlighting key elements in an unknown sample.

Parupelli and Desai performed EDS on hybrid additive manufacturing samples in 2020 to map the uniformity of components utilizing a carbon and nano silver matrix cured by a laser [33]. The work showed the possibility of manufacturing functionally gradient materials for implementation in electronic components using additive fabrication methods.

Focused Ion Beam (FIB) milling involves the removal of material from a sample by the sputtering of incident ions, normally Gallium ions [34]. Unlike standard microscopy addons, FIB is a destructive technique that physically slices into a substrate to determine either cross sectional composition, or morphology. Ions are bombarded into a hyper focused area on a substrate to grind the material away. A common real-world comparison includes sandblasting of surfaces, especially as a post-processing method of additive manufacturing, to remove debris or rough patches from the surface of the component.
In 2021, Rasnasingha et al performed focused ion beam milling on barium strontium titanate samples fabricated via aerosol jet printing for implementation in radio-frequency applications [35]. The work showed various characterization methods utilizing focused ion beam milling including surface and cross-sectional morphology.

In 2023, Gabbet et al. performed scanning focused ion beam nanotomography to characterize the morphology of aerosol jet printed components comprised of graphene, tungsten silicon disulfide, and silver nanostructured networks [36]. The work explored the creation of a methodology for the collection of morphological data to be used in print optimization.

This work employed the use of stylus profilometry, optical microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and focused ion beam milling to characterize samples after analysis and testing.

1.11. Approach

This study involves the complete additive manufacturing process of a novel silver ink. Sample fabrication is discussed. Optical microscopy, scanning electron microscopy, and focused ion beam images are employed to determine validity of recorded data. Average resistivity and thermal coefficient of resistance values are calculated with confidence intervals.

1.12. Overview and Contributions

This document is divided into chapters. Chapter one focuses on and provides all necessary background information required to understand the work performed in this study. Chapter two will focus on the additive manufacturing process and experimental methodology employed for fabrication of samples. Chapter three will cover the results of experimental procedures, providing
discussion and rationale. Lastly, chapter four will provide a summary of the work performed, as well as suggestions for future research.

The contributions of this study are four-fold. This study aims to determine optimal print parameters for the fabrication of printed silver traces. Additionally, the determination of optimal post-processing methods of fabricated silver conductive traces. This work also aims to provide insight into the effects of print and post-processing methods on microstructures found in printed traces. Lastly, this study aims to determine the effect of application conditions, in the form of temperature, on strain sensitivity. These four contributions serve to complete an overarching goal. That goal is to characterize and compare a novel ink formulation provided by ElectronInks by determining optimized printing and post-processing parameters, to implement the ink formulation into electronic devices.
II. Experimental Procedure

The following section discusses the methods and steps taken to design and fabricate samples for analysis and microscopy as well as the materials selected to complete this study.

2.1. Material Selection

The following materials were selected to complete this study: ElectronInks formulation EI-616, ElectronInks formulation EI-615, and Novacentrix JS-A221AE.

2.1.1. ElectronInks EI-615

ElectronInks formulation EI-615 is a particle free proprietary novel ink formulation composed of a silver metal salt complex designed for aerosol jet printing. While most of its information is currently kept a trade secret as the ink has not been released for commercial use, its use as an aerosol ready ink for aerosol jet printing for the fabrication of electronic components highlight it as being of interest for the purpose of this study.

2.1.2. ElectronInks EI-616

Formulated as a “sister” ink to EI-615, EI-616 is also a particle free proprietary novel ink formulation composed of a silver metal salt complex designed for aerosol jet printing. The primary difference, by word of ElectronInks, is that EI-616 attempts to solve some of the ability gaps of EI-615 with a larger amount of adhesion promoter added to the formulation to assist in printing on a much wider range of substrates. This ink is the primary focus of this work.
2.1.3. Novacentrix JS-A221AE

Novacentrix JS-221AE is a commercially available ink formulation developed by Novacentrix that possesses good adhesion to a wide variety of substrates as well as several desirable material properties for a particle-based ink [37].

2.2. Digital Fabrication Procedures.

To fabricate physical components for testing, additive manufacturing practices shown below dictate that the part be designed digitally before any printer is capable of production.

![3D Printing Process](image)

*Figure 9: Process for additive manufacturing [38]*

This process is available to any computer aided design software that can export created digital drawing files as program files (.prg) or stereolithography files (.stl) which are readable sets of instructions by a chosen printer. The selection of digital software ultimately is up to the user’s ability or level of comfort with the selected software. For this study, the digital creation of drawing files and subsequently generated program files was accomplished with AutoCAD design software with a virtual masking toolbox installed to assist in creating solidified shapes.

To begin designing parts for fabrication in AutoCAD, users need to define the unit system utilized to ensure the printer receives correct directions and dimensions. Using the
“units” command, a list of unit systems can be selected ranging from angstroms to lightyears shown in figure 2.2. All measurements used for this work are in millimeters.

![Drawing Units](image)

**Figure 10: Unit selection window in AutoCAD**

After defining a unit system, initial outlines of components can be generated. These were performed using AutoCAD’s “rectangle” command, followed by inputting points to set the length and width of each shape. Figure 11 shows the resulting design.

![Outline of samples in AutoCAD software](image)

**Figure 11: Outline of samples in AutoCAD software**
These initial setup shapes lay the groundwork for fabricating conductive pads. However, at this stage, the digital sample is comprised of a collection of single dimension lines to form rectangular shapes. A chosen printer will not create a two-dimensional pad automatically unless it has instructions to print into designated locations. To achieve this, AutoCAD has a toolbox for video masking that can be accessed using the “vmtools” command. This command brings up additional settings shown in figure 12 to easily fill out shapes defined by the user including angle of fill, spacing between fill lines, and other user desired functions.

![vmTools window](image)

*Figure 12: vmTools window*

For the purposes of this study, the serpentine fill tool as well as the trace width general settings were utilized. All other settings were kept to their default.
Using these tools, all sample outlines were filled in, resulting in figure 14. The end result, referred to as a “tool path”, is a two-dimensional rectangle that carries the proper instructions for a selected printer to perform and generate the desired shape. Outlines of samples were selected using the serpentine settings, creating samples that were filled with a single serpentine line horizontally at a 20-micron spacing. This trace width was kept consistent between all printed substrates. Digital samples were then exported using virtual masking tool to create an executable program file able to be uploaded into a printer. These files were then utilized to fabricate all conductive trace samples.
Using the same process above, a secondary set of samples were produced, creating an identical toolpath at a 90-degree angle to the shown horizontal serpentine path. These program files were used to perform laser sintering on printed samples of the same shapes.

*Figure 14: Sample pads filled with serpentine pattern (top) with closeup on serpentine line (bottom)*

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2.3. Printing

All prints were conducted on one inch cut glass microscope slides. Substrates were washed using acetone, methanol, and isopropanol before drying with a pressurized nitrogen gas. Samples were also oxygen plasma treated using an nScrypt 3dn-300 shown below, before being loaded into the OPTOMEC Aerosol Jet 200 printer.

![Figure 15: nScrypt 3Dn series printers with 300 model (far left) [39]](image)

Using generated program files created in AutoCAD, two sets of samples were prepared. Sample set one was comprised of several design iterations, ultimately resulting in five 3 by 6-millimeter pads on a 1-inch glass slide. Sample set two was comprised of one 20 by 4-millimeter pad on a 1-inch glass slide. These sample sets were printed using ElectronInks formulations 615 and 616 along with Novacentrix JS-A221AE using print parameters conducive to steady state printing. This involved tailoring the sheath, atomization pressure, and atomization current to each ink, accounting for ambient conditions as well as the stability of the ink formulation. All printing was performed at a print speed of 2mm/sec.
2.3.1. ElectronInks EI-616

Samples fabricated with ElectronInks formulation EI-616 were subject to several design generations to address issues during the fabrication process. Generation one samples were printed in two steps. Step one was the creation of five single traces using Novacentrix JS-A221AE silver ink shown in figure 16 using the previous digital creation steps.

![Generation one AutoCAD drawings](image)

*Figure 16: Generation one AutoCAD drawings*

Samples of Novacentrix traces were printed in batches of five substrates. The five single traces after printing were then thermally sintered at 200°C for one hour before being returned to the printer. ElectronInks EI-616 was printed in a thin trace of 19x4.5mm across the previously
sintered traces to create a conductive path over each of the five prepared substrates. Figure 17 shows a resulting print of a generation one sample.

To address reliability issues in generation one samples, sample ordering was employed. Samples were numbered after Novacentrix was deposited onto substrates surface, and this order was maintained as traces of EI-616 were applied. Sample ordering is shown below in Figure 18.
To further address durability issues within generation one and two samples, generation three samples were developed. Generation three samples consisted of several 3x6mm pads printed directly with ElectrionInks EI-616.

Generation three samples were printed using a sheath pressure of 25-60 SCCM (0.10 – 0.41PSI), an atomization pressure of 7-20 SCCM (0.17 - 0.31PSI), and an atomization current of
0.201 – 0.387 mA, based on ambient conditions and ink stability. A chiller was also connected to the printer during printing set to 18-20°C in accordance with ambient conditions.

2.3.2. ElectronInks EI-615

Samples fabricated with ElectronInks EI-615 formulation were produced using the generation three tool path developed with EI-616. Samples were printed using using a sheath pressure of 50 SCCM (0.13 PSI), an atomization pressure of 7 SCCM (0.29 PSI), and an atomization current of 0.303 – 0.326 mA, based on ambient conditions and ink stability. A chiller was also connected to the printer during printing set to 25°C in accordance with ambient conditions.

2.3.3. Novacentrix JS-A221AE

Samples fabricated with Novacentrix JS-A221AE formulation were also produced using the generation three tool path developed with EI-616. Samples were printed using using a sheath pressure of 80 SCCM (0.52 PSI), an atomization pressure of 25 SCCM (0.67 PSI), and an atomization current of 0.310 – 0.430 mA, based on ambient conditions and ink stability. A chiller was also connected to the printer during printing set to 25°C in accordance with ambient conditions.
2.4. Laser Sintering

Printed conductive traces were removed from the OPTOMEC Aerosol Jet 200 printer and transferred into an OPTOMEC Aerosol Jet 300 printer for sintering. Samples fabricated for resistivity measurements were sintered with a 20µm spot size 830nm laser at a 5mm/sec scanning speed utilizing the same 20µm path separation found in the printing program files. For samples fabricated with ElectronInks EI-616 samples were sintered at laser powers ranging from 60 milliwatts to 140 milliwatts at a 90 degree angle to the print direction at increments of 20mW between laser powers. For samples fabricated with ElectronInks EI-615 samples were sintered at laser powers ranging from 60 milliwatts to 200 milliwatts at a 90 degree angle to the print direction. For a sample fabricated with Novacentrix JE-A221-AE samples were sintered at laser powers ranging from 60 milliwatts to 140 milliwatts at a 90 degree angle to the print direction. Additionally one sample of each ink was sintered thermally at 200 degrees Celsius for one hour each.

Samples fabricated for temperature coefficient of resistance measurements were sintered with a 20µm spot size 830nm laser at a 5mm/sec scanning speed at a constant laser power of 100mW at a 90 degree angle to the print direction. Table 4 shows a summary of sintering conditions utilized in this study.
2.5. Etching and Post-processing

After printing and sintering conductive pads with a laser, each sample can have residual unsintered material left behind. To remove unsintered ink, samples were etched via 1-Dodecene, acetone, methanol, and isopropanol to leave only sintered silver traces behind. Samples fabricated with ElectronInks ink formulations after sintering were washed with wafer bond remover (1-Dodecene), followed by acetone, methanol, and isopropanol before drying with nitrogen gas. This process is not applicable to Novacentrix ink formulations. This is due to Novacentrix being a water-based ink, samples fabricated with Novacentrix ink formulations were not washed with solvents after printing.

<table>
<thead>
<tr>
<th>Ink Formula</th>
<th>Restivity Measurement Laser Power</th>
<th>TCR Measurement Laser Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>ElectronInks EI-615</td>
<td>60, 80, 100, 120, 140, 160, 180, 200mW</td>
<td>100mW</td>
</tr>
<tr>
<td>ElectronInks EI-616</td>
<td>60, 80, 100, 120, 140mW</td>
<td>100mW</td>
</tr>
<tr>
<td>Novacentrix</td>
<td>60, 80, 100, 120, 140mW</td>
<td>100mW</td>
</tr>
</tbody>
</table>

*Table 4: Summary of sintering conditions*
2.6. Resistivity Measurements

Sintered conductive traces containing a multi-pad setup were connected to a four-point probe setup using a Keithley 2420-C3A source meter to conduct resistivity measurements. Resistance measurements were taken using the Keithley source meter on each sintered conductive pad.

For temperature coefficient of resistance measurements, silver paste was mixed using equal parts of a two-component silver epoxy. This epoxy was applied to the single printed conductive trace along with a thin copper wire and then set on a hot plate to cure at 100 degrees Celsius for 10 minutes. These paths were then connected to a similar four-point probe using a Keithley 6221 DC and AC current source, a Fluke 289 true RMS multimeter and an H306A Omega data logger thermoset on top of a PMC 730 series hot plate. A constant current of 1 milliamp was applied to the sample and voltage measurements were taken at room temperature. Samples continued to be subjected to voltage measurements at increasing temperature steps of 10 degrees Celsius from 30 to 100 degrees Celsius. Voltage measurements were again taken at decreasing temperature steps of 10 degrees Celsius from 100 degrees to room temperature.

Figure 20: Four-point probe setup
2.7. Profilometry

Samples were then transported to a DektakXT profilometer and topographically analyzed for pad thickness to obtain resistivity data. Profilometry was performed on samples to calculate resistivity of printed silver traces.

Figure 21: TCR setup

Figure 22: DektakXT profilometer [40]

Samples were loaded and aligned with the stylus using user defined alignment shown in figure 23.
Samples were then analyzed using a hill and valley scan, utilizing a stylus force of 3mg for a duration of 60 seconds over a length of 3500µm. Data was then leveled and then exported as a Microsoft Excel file to be imported into MATLAB for calculations of cross-sectional area.

2.8. Additional Procedures

Additional samples of each sample set were fabricated for study through optical microscopy, scanning electron microscopy, and focused ion beam procedures. Optical images
were taken using a Keyence VK-X1000 using confocal lighting at magnifications of 5x and 10x to acquire detailed surface images of fabricated samples.

Scanning electron microscopy was performed using both a Hitachi Su-70 SEM and a FEI Helios G4 SEM/FIB to acquire detailed surface images of fabricated samples as well as EDS data of different samples. Samples comprised of EI-616 were also sectioned using the FIB tool to obtain cross sectional area data.
III. Results and Discussion

The following section covers the raw data collected as a result of the study along with necessary ranges and confidence intervals in addition to discussion to the effects of these measurements.

3.1. Print Parameters

Print parameters were tuned during the duration of the experiment. Samples fabricated with ElectronInks EI-615 showed the best printing stability with a sheath pressure of 50 SCCM (0.13 PSI), an atomization pressure of 7 SCCM (0.29 PSI), a chiller setup of 25°C, and an atomization current of 0.303mA to 0.326mA depending on ambient and ink conditions. Samples fabricated with ElectronInks EI-616 showed the best printing behavior with a sheath pressure between 25 - 60 SCCM (0.10 - 0.41 PSI), an atomization pressure between 7 - 20 SCCM (0.17 - 0.31 PSI), a chiller setup ranging between 18 and 20°C, and an atomization current of 0.201mA to 0.387mA, heavily depending on ambient temperatures and ink conditions. Samples fabricated with Novacentrix JS-A221AE showed the best printing behavior with a higher sheath pressure of 80 SCCM (0.52 PSI), an atomization pressure of 25 SCCM (0.67 PSI), a chiller setup set to 25°C, and an atomization current of 0.310mA to 0.430mA depending on ambient temperatures and ink conditions. These parameters were determined to produce optimal conductive traces via an OPTOMEC Aerosol Jet 200 printer in accordance with outside factors and conditions as well as stability of the printing medium. Table 5 shows a summarized set of print parameters utilized during the study.
3.2. Resistivity Measurements

The following section covers the results of resistivity measurements taken during this study. For the purposes of this work, resistivity measurements refer to “bulk” as the resistivity of bulk elemental silver, $1.59 \times 10^{-8} \, \Omega \cdot m$. A common practice in the additive manufacturing community is to refer to resistivity values in the form of ‘times bulk resistivity’. An example sample with an average resistivity measurement of $1.59 \times 10^{-7} \, \Omega \cdot m$ would be referred to as 10x bulk resistivity. This study refers to all resistivity measurements as “times bulk resistivity” for convenience.

3.2.1. ElectronInks EI-616

ElectronInks formulation EI-616’s test structures underwent several design generations to account for reliability and durability issues during the printing and analysis process of this work. Generation one samples were subject to an overall process of Novacentrix printing, thermal sintering, ElectronInks printing, and laser sintering in a randomized sample order. Samples were not laser sintered in the order they were printed in. Figure 25 shows the data collected from generation one samples fabricated with ElectronInks EI-616.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Sheath Pressure</th>
<th>Atomization Assembly Pressure</th>
<th>Atomization Current</th>
<th>Chiller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Inks EI-615</td>
<td>50 SCCM - 0.13 PSI</td>
<td>7 SCCM - 0.29 PSI</td>
<td>0.303 - 0.326 mA</td>
<td>25°C</td>
</tr>
<tr>
<td>Electron Inks EI-616</td>
<td>25 - 60 SCCM 0.10 - 0.41 PSI</td>
<td>7 - 20 SCCM 0.17 - 0.31 PSI</td>
<td>0.201 - 0.387 mA</td>
<td>18 - 20°C</td>
</tr>
<tr>
<td>Novacentrix JS-A221AE</td>
<td>80 SCCM - 0.52 PSI</td>
<td>25 SCCM - 0.67 PSI</td>
<td>0.310 - 0.430 mA</td>
<td>25°C</td>
</tr>
</tbody>
</table>

*Table 5: Optimized printing results*
It was found that with randomized samples, obtaining a reliable set of data would be challenging, and that collected data had wide variation as shown by the error bars generated by MATLAB. The resistivity of generation one samples varied between 25x and 5000x bulk silver resistivity. The wide variety in sample resistance could be a result of the interaction between the ElectronInks and Novacentrix formulations on the substrate being processed with different methodology. It was found during sample fabrication that ElectronInks EI-616 has several stability issues regarding its shelf life. Assemblies prepared with EI-616 were required to be utilized within 24 hours, otherwise any print parameter settings would no longer be viable, and the fabrication of reliable samples would be infeasible. This wide variation and instability could be the result of the formulation process of ElectronInks EI-616. This ink formulation is not
commercially available for printing and is developed in small batches compared to other more commercially available formulations. As such, it is subject to large amounts of variation from batch to batch.

Addressing reliability issues, generation two samples were produced, followed by generation three samples to address durability issues. These samples were kept in strict order or printed to ensure consistency in printing. Figure 26 shows the results of generations two and three resistivity data.

![Figure 26: Generation two and three resistivity data](image)

The resistivity of generations two and three varied between 25x and 75x bulk resistivity. To optimize post-processing parameters over several laser powers for sintering, it was found in all generations of EI-616 samples that a laser power of 100mW would produce the lowest resistivity values for fabricated samples. This was confirmed by plugging raw data into MATLAB and utilizing the built in curve fitting tool to generate a 2nd degree polynomial.
curve across the data. Each curve fit had the global minimum at an x-coordinate of 100mW laser power.

3.2.2. ElectronInks EI-615

Samples fabricated with ElectronInks EI-615 utilized the design of third generation EI-616 samples to ensure reliability and durability conducive to analysis. EI-615 shared similar stability issues with EI-616, with ink consistency lasting for 24 hours after atomization assembly was prepared. Figure 27 shows the resistivity measurements collected for EI-615.

![Figure 27: Resistivity data collected for EI-615](image)

Samples collected for EI-615 showed a much higher consistency per sample, with averages deviating no more than 0.042 times bulk resistivity at a laser power of 60mW. The overall data however does vary widely, ranging from 35x to 7x10⁶x bulk resistivity. This wide deviation could be a result of the formulations specifications. EI-615 was designed to adhere extremely well to a dielectric layer of Benzocyclobutene (BCB) which is a photosensitive
polymer with the chemical formula C$_8$H$_8$ and is widely utilized for microelectronic and photonic applications [41]. BCB has difficulty adhering to glass, requiring more laser power to be applied to assist in adhering the jetted material to the substrate. A closer inspection of the figure between 160mW and 200mW laser power would indicate an optimal parameter of 180mW sintering conditions prior to post-processing and measurements resulting in an average resistivity of ~35x bulk. Figure 28 shows this trend with the graph’s inflection point at 180mW.

![Graph: Effect of Laser Power on Factor of Resistivity in Aerosol Jetting of Electron Inks EI615 on Glass](image)

*Figure 28: Resistivity data of EI-615 sintered at 160mW to 200mW*
3.2.3. Novacentrix JS-A221AE

Samples fabricated with Novacentrix formulated inks also utilized the generation three design developed for EI-616. Compared to the other two studied formulations, Novacentrix JS-A221AE did not share the same shelf life and ink stability issues found in formulations provided by ElectronInks. Figure 29 shows the resulting resistivity measurement data obtained.

![Effect of Laser Power on Factor of Resistivity in Aerosol Jetting of Novacentrix JS-A221AE on Glass](image)

*Figure 29: Novacentrix resistivity*

The collected data shows a resistivity factor of 25x to 40x is obtainable under current experimental procedures. During calculation, a laser power of 100mW was shown to produce samples with the highest resistivity factor. Upon comparison, statistical analysis, and applying Chauvenet’s criterion [42] to the results indicates that the collected data at 100mW laser power is an outlier and is outstanding enough to be disregarded from the sample set. Upon the removal of the outlying datapoint and applying MATLAB’s curve fitting tool to the data, the fitted curve indicates the sintering condition of 100mW laser power is an optimal setting.
Chauvenet’s criteria is a statistical criterion for the determination of outliers in a set of data by identifying data points that have a low statistical chance of occurring. An outlier is a data point that falls outside the realm of occurring realistically in a data set. For small data sets this can be applied using equations 13 and 14 shown below.

\[ z_0 = \left| \frac{x_i - \bar{x}}{s_x} \right| \] (13)

\[ \left( 1 - 2 \times P(z_0) \right) < \frac{1}{2} N \] (14)

In equation (top) \( x_i \) is the value of a potential outlier of a set of \( N \) datapoints, \( \bar{x} \) is the sample average or mean, and \( s_x \) is the standard deviation of the data set. These values calculate \( z_0 \) which is the maximum allowable deviation from the average. This value is then compared to the sample size. If the calculated value of the left side of equation (bottom) is less than half the sample size, the data is considered an outlier and can be discarded. For large data sets, this criterion can be applied to data points falling outside of the three standard deviation metric [36].
3.3. Temperature Coefficient of Resistance Measurements

The following section covers the results of temperature coefficient of resistance measurements taken during this study.

3.3.1. ElectronInks EI-616

Figure 30 shows the raw data collected from TCR measurements taken on three separate samples fabricated with EI-616 sintered with a laser power of 100mW along with the trend lines calculated for both heating and cooling cycles.

Table 6 shows a summary of the data presented in the figure, along with standardized statistical data.
Table 6: Summarized data of EI-616 TCR measurements

<table>
<thead>
<tr>
<th>Samples</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>Average</th>
<th>Standard Dev.</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Cycle</td>
<td>0.001964</td>
<td>0.002088</td>
<td>0.001889</td>
<td>0.00198</td>
<td>0.000082</td>
<td>0.001980 ± 0.000082</td>
</tr>
<tr>
<td>Cooling Cycle</td>
<td>0.001777</td>
<td>0.002019</td>
<td>0.001721</td>
<td>0.001839</td>
<td>0.000129</td>
<td>0.001839 ± 0.000129</td>
</tr>
</tbody>
</table>

Samples of EI-616 showed an average $\alpha$ value of 0.001980 1/C° for the heating cycle and an average value of 0.001839 1/C° for the cooling cycle. These measurements are bound with a 95% confidence interval of 0.001980 ± 0.000082 1/C° and 0.001839 ± 0.000129 1/C° to the heating and cooling cycles respectively.

The confidence interval is a measurement of spread in each data set. The value associated with the percentage is representative of what percent of the overall data will fall between the listed bounds [43]. Common confidence intervals are 90%, 95%, and 99% with the spread widening as the percentage increases. A confidence interval can be calculated using equation 15.

$$95\% \, CI = \frac{t \cdot s}{\sqrt{n-1}} \quad (15)$$

In the equation, $n$ is the sample size, $s$ is the sample set standard deviation, and $t$ is a predetermined value associated with a standardized statistical table. Standard deviation can be calculated using equation 16.

$$\sigma = \sqrt{\frac{\sum(x - \mu)^2}{N}} \quad (16)$$

3.3.2. ElectronInks EI-615

Figure 3 shows the raw data collected from TCR measurements taken on three separate samples fabricated with EI-615 sintered with a laser power of 100mW along with the trend lines
calculated for both heating and cooling cycles. Samples of EI-615 had a larger variation from calculated trend lines compared to EI-616.

![TCR Measurement of EI-615 on Glass, 100mW Laser](image)

**Figure 31: TCR data of EI-615**

Table 7 also shows a summary of raw data collected for EI-615, along with continued standardized statistical data.

![Table 7: Summarized TCR data of EI-615](image)

3.3.3. Novacentrix JS-A221AE

Figure 32 shows the raw data collected from TCR measurements taken on three separate samples fabricated with EI-615 sintered with a laser power of 100mW along with the trend lines.
calculated for both heating and cooling cycles. Samples of Novacentrix had the largest deviations from calculated trend lines as well as $\alpha$ values closest to the literature value of 0.0034 [22].

![TCR Measurement of Novacentrix JS-A221AE on Glass, 100mW Laser](image)

*Figure 32: TCR graph of Novacentrix*

Table 8 contains a summary of the data presented in Figure 3.8.

<table>
<thead>
<tr>
<th>Novacentrix JS-A221AE $\alpha$ values</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>Average</th>
<th>Standard Dev.</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Cycle</td>
<td>0.002513</td>
<td>0.004142</td>
<td>0.003707</td>
<td>0.003454</td>
<td>0.000689</td>
<td>0.003454 ± 0.000779</td>
</tr>
<tr>
<td>Cooling Cycle</td>
<td>0.002524</td>
<td>0.002294</td>
<td>0.009138</td>
<td>0.004652</td>
<td>0.003173</td>
<td>0.004652 ± 0.003173</td>
</tr>
</tbody>
</table>

*Table 8: Summary of Novacentrix TCR data*

Novacentrix had the widest variation of data from the calculated trend lines as well as an average TCR value closest to the accepted value of $\alpha$ for silver.
3.4. Optical Microscopy

The following section covers optical microscopy images taken during the study as well as discussion pertaining to the collected images.

3.4.1. ElectronInks EI-616

Optical images were collected from an untested sample fabricated with EI-616 and laser sintered to accommodate several different laser powers onto one substrate for efficiency in microscopy practices. Figure 33 contains a collection of images collected on a glass substrate containing laser sintered pads of EI-616.
Figure 33: Optical images of EI-616, sintered at varied laser powers
Optical images of EI-616, starting with 60mW laser and progressing to 140mW get visually darker as the laser power increases. This is coupled with a surface image that appears more textured with progressing sintering power. Laser sintering applies a localized heating region that interacts with the sample in one of two ways. Sintering at too low of a power does not fully sinter the desired material leaving unsintered material behind to be removed during the solvent wash step. Sintering at too high laser power creates bubbles underneath the surface from rapid heating and material expansion.

3.4.2. ElectronInks EI-615

Optical images were collected of an untested sample fabricated with EI-616 and laser sintered to accommodate several different laser powers onto one substrate for efficiency in microscopy practices. Figure 34 contains a collection of images collected on a glass substrate containing laser sintered pads of EI-615.
Figure 34: Optical images of EI-615
The captured EI-615 optical images are difficult to distinguish from one another aside from the lowest laser power sintering pad at 60mW. All samples appear very similar aside from minor artifacts found during imaging on samples sintered at 120mW, 140mW, and 160mW.

3.4.3. Novacentrix JS-A221AE

Optical images were collected of an untested sample fabricated with EI-616 and laser sintered to accommodate several different laser powers onto one substrate for efficiency in microscopy practices. Figure 35 contains a collection of images collected on a glass substrate containing laser sintered pads of Novacentrix.
Figure 35: Optical Images of Novacentrix JS-A221AE
Images captured of Novacentrix appear to get lighter in color as laser power increases. Samples also show a set of vertical lines at seemingly consistent intervals across the sample surface. During the printing process, samples may not be completely aligned with the printer’s coordinate grid. To account for the variance, fiducial alignments are made to give the printer the corrective angle to print or laser sinter with. These vertical lines could be the result of the printer adjusting for the fiducial alignment intermittently to ensure the sample is “in line” with the printer.

3.5. Scanning Electron Microscopy

The following section covers images collected using two scanning electron microscopes to collect images of studied ink formulations.

3.5.1. ElectronInks EI-616

Scanning electron microscopy was performed using a Hitachi SU-70 SEM at a 5kV beam voltage and 15.9mm working distance. Samples showed consistent surface morphology regarding electrical resistance measurements. Low laser power EI-616 samples at 2500x magnification show high porosity on the surface. The amount of porosity lowers as samples approach 100mW laser power then increases again as laser power exceeds 100 milliwatts. 140mW laser power sintering EI-616 images show large cracks on the surface. Figure 36 shows the evolution of samples from low to high laser power.
3.5.2. ElectronInks EI-615

Images of EI-615 were collected via scanning electron microscopy. Similar to their optical images, it is difficult to differentiate between them at a glance. The samples all appeared smooth with minimal defining surface features. Because of the issue of adhesion on glass, samples may be extremely thin and are not built up enough to possess more detailed morphology.
3.5.3. Novacentrix JS-A221AE

Scanning electron microscopy images of Novacentrix JS-A221AE show high amounts of porosity, with increased porosity as laser power increases shown in figure 38.

![SEM Images of Novacentrix JS-A221AE](image)

Figure 38: SEM Images of Novacentrix JS-A221AE

3.6. Focused Ion Beam

Focused ion beam milling was performed on samples fabricated with ElectronInks EI-616. Attempts were made to complete FIB work on all fabricated samples, however, due to schedule constraints and equipment maintenance, EI-616 was the only sample set to have a FIB study conducted. Figure 39 shows the cross sections of EI-616 at 60mW, 100mW, and 140mW laser powers.
Samples saw delamination occur in samples sintered at 60mW. This is due to the laser power being too weak and not penetrating the sample deep enough to completely sinter. Unsintered material was left behind and after a solvent wash, was removed from the sample, leaving behind large open pockets that affected both the microstructure and electronic properties. Samples sintered at 140mW saw a similar delamination phenomenon, however, because the laser power was set too high, the laser would over penetrate the sample. This would create air bubbles underneath the sample surface which with the expansion of the material due to heat, would cause thermal cracking on the surface, and overall sample. This in turn would affect the electrical properties of the sample by creating longer paths for current to flow.
IV. Summary and Conclusions

Characterization of aerosol jet printed silver thin films sintered by a scanning laser has been conducted. Samples were fabricated using different print and post-processing parameters to optimize a methodology for printing.

Methodology for the complete additive manufacturing process of ElectronInks EI-616 was outlined. It was determined that samples fabricated with ElectronInks EI-616 showed the best printing behavior with a sheath pressure between 25 - 60 SCCM (0.10 - 0.41 PSI), an atomization pressure between 7 - 20 SCCM (0.17 - 0.31 PSI), a chiller setup ranging between 18 and 20°C, and an atomization current of 0.201mA to 0.387mA would produce the most reliable silver traces.

Post-processing parameters for ElectronInks EI-616 were also outlined, indicating a laser sintering condition of 100mW laser at 5mm/sec would produce silver traces with the lowest resistivity for use in electronic components.

Next steps in this research would be to vary other steps of the fabrication process including laser scanning speed to determine a full set of optimal parameters for the fabrication of electronics utilizing this particular ink formulation.

Another step would be to perform reliability testing on samples printed with ElectronInks EI-616 in the form of fully realized electronic components to determine their mechanical and electrical strengths in varied conditions before being manufactured into packaged electronics. This would allow for a complete dataset of optimized parameters to report to ElectronInks to provide with large scale batches to ensure commercialized ink takes the form of other additive
components in which materials become “plug and play” with little to no tuning on the part of the consumer or research group.
Work Cited


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