Photonic sintering of nanoparticles is a relatively new process for sintering of nanoparticles, deposited on a substrate, into functional solid structures. The working principle of this process is the incidence of large-area broad-spectrum light onto deposited nanoparticles, which results in heat generation in the nanoparticles and their subsequent densification. Key advantages of photonic sintering include rapid, scalable and ambient condition operation. For these reasons there is significant interest in using this process as a manufacturing solution for nanoparticle sintering in emerging applications like RFID tags, flexible electronics, solar cells, and sensors. Despite preliminary demonstrations of photonic sintering, there is little knowledge on the underlying process physics, which results in limited physics-based control of the process. The goals of this work are to (1) expand the state of knowledge on the physics of photonic
sintering; and (2) develop a system that can leverage the advantages of photonic sintering for low-cost additive manufacturing using nanoparticle building blocks.

Four key topics in photonic sintering are investigated. First, the effects of nanoparticle size on densification and the temperature (of deposited nanomaterial and substrate) are experimentally characterized. Both the temperature and nanoparticle densification are found to be highly dependent on the nanoparticle sizes used. Secondly, a multiphysical model of photonic sintering is developed to link particle size, optically-induced heat generation, resulting temperature rise and consequent interparticle necking. In addition to reflecting experimentally observed trends, the developed model also provides an improved understanding of the underlying physics behind photonic sintering. Thirdly, densification and temperature evolution in photonic sintering of non-metallic nanoparticles is characterized.

Lastly, photonic sintering and inkjet deposition are combined into one system to demonstrate the potential of using photonic sintering for a low-cost, multi-material, desktop additive manufacturing system. With further hardware and software development and greater understanding of the physics behind photonic sintering, the developed additive manufacturing system can be further refined. Further development and commercialization of the system developed here has the potential to increase accessibility of low-cost, multi-material additive manufacturing (metals, semi-conductors and ceramics) similar to the currently increased accessibility of polymer 3D printing.
Photonic Sintering of Nanoparticle Inks: Experimental Characterization, Computational Modeling and System Design for Additive Manufacturing

by

William D. MacNeill

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Dean of the Graduate School

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William D. MacNeill, Author
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CONTRIBUTION OF AUTHORS

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Chapter 1: Introduction

1.1 Socio-economic motivations

Deposition and densification of nanoparticles on substrates is used in manufacturing a variety of devices for many emerging applications. For example, conductive metallic nanoparticles can be deposited and sintered to create flexible interconnects between functional electronic devices in flexible electronics. Conductive oxides like Indium-Tin-Oxide (ITO) are used functional thin-film layers in sensors and solar cells. Copper-Zinc-Tin-Sulphide (CZTS) can be used in place of rare earth metal compounds as an absorber layer in solar cells, reducing the cost of solar cells considerably. Additional proven or proposed applications include antennas/RFID tags [1], photovoltaic cells [2, 3], displays [4-6], electrical components [6] (such as capacitors and rectifiers [7], multilayer ceramic capacitors [8], logic and memory components [1], organic thin film transistors [6, 7], organic LEDs [9]), magnetic devices [8], printed/Flexible electronics [7, 10], and wearable electronics [4, 11].
Table 1.1: Overview of applications for patterned and continuous thin-films

<table>
<thead>
<tr>
<th>No</th>
<th>Technology</th>
<th>Market pull</th>
<th>Manufacturing requirements</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>RFID, Flex. electronics</td>
<td>$10 Billion by 2017</td>
<td>Maximize material density &amp; control pattern geometry in large area manufacturing (Figure 1.1a).</td>
<td>[12]</td>
</tr>
<tr>
<td>A2</td>
<td>Environmental sensors</td>
<td>$1.7 Billion by 2020</td>
<td>Control porosity to between 2-50 nm for large area deposition (Figure 1.1b).</td>
<td>[13-17], [18]</td>
</tr>
<tr>
<td>A3</td>
<td>Smart windows</td>
<td>1.3 Billion by 2015</td>
<td>Reduce manufacturing cost from $1000/m² to &lt;few $100/m² (Figure 1.1c) for large area deposition.</td>
<td>[19-22], [23]</td>
</tr>
<tr>
<td>A4</td>
<td>Flexible solar cells</td>
<td>Growth in solar power demand by 3-4 times from 2012-2017</td>
<td>Move away from rare earth element based semiconductors. Large area, high throughput, low-cost thin-films</td>
<td>[12, 17, 24-27]</td>
</tr>
</tbody>
</table>

Figure 1.1:(a) Antenna for RFID tag [28] (b) Image of mesoporous metal oxide film for gas sensor [29] (c) Smart window components [30] (d) CZTS based solar cell (e) nanostructured ZnO antireflective layer [31].

Thin-film RFID tags and flexible electronics (row A1) have significant potential in pervasive sensing, internet of things and wearable electronics devices [12, 14, 20, 32]. Antennae or interconnects (Figure 1.1a) made by sintering metal nanoparticles like Ag and Cu into patterns are key components of these devices. Such patterns are typically a few 100 microns in width and thickness. Thin-films of semiconducting oxides like SnO₂ and ZnO with tailored pore sizes between 2 to 50 nm [12], shown in Figure 3b, are key elements of
gas sensing and environmental monitoring devices ([14, 15] and row A2). Smart windows (row A3) have significant potential to create energy savings in built environments [17, 19,20]. A key component of these devices is a transparent conductive layer of metallic nanowires or conductive oxides like ITO [21, 23] on large-area flexible polymeric substrates to function as current carrying electrodes (Figure 3c). Thin-film flexible solar cells use continuous semiconductor thin-films (Figure 3d, row A4) of materials like Copper Zinc Tin Sulfide (CZTS), CdTe and Copper Indium Gallium Selenide (CIGS) as light absorber layers [17, 25, 33, 34]. Elements like Indium and Cd are, however, rare earth elements and have major demands from the display and optical devices industry. So, the use of semiconductors like CZTS is preferable [26-28, 35, 36] and the potential of CZTS as an absorber layer in flexible solar cells has been shown [28-31]. Solar cells also use metallic films as conductive contacts (Figure 3d).

Conventional 3D additive manufacturing uses polymeric, non-polymeric and composite microparticles and densifies them into 3D structures. While additive manufacturing of polymers has developed to the stage where machines can be bought and used at home, metals additive manufacturing has not made this transition yet. The most common process used for additive manufacturing of metals, i.e., Selective Laser Sintering (SLS) requires an expensive machine which carries a large volume of metallic powder in a bed. Direct Metal Deposition (DMD) does not need a bed, but suffers from the inability to make parts that need a support. However, both these systems are very expensive (a few 100K at the minimum) and are out of the reach of individuals, communities and sometimes
even industries. The development of a low-cost, desktop and multi-material-capable (non-polymer) additive manufacturing process with the additional capability to tailor material composition from the nanoscale level upwards can significantly magnify the potential impact of additive manufacturing. As shown in chapter 5, the development of a system with concurrent deposition and photonic sintering of nanoparticle-inks may provide such a solution.

1.2 Technological drivers

A common factor in the above applications is that nanoparticles need to be deposited, followed by a sintering step in which the deposited nanoparticle ensemble is densified by heating. The use of nanoparticle-inks (i.e., colloidal suspensions of nanoparticles) as a conduit for delivering the nanoparticles to the substrate offers significant advantages over vacuum deposition, electrochemistry and sol-gel routes due to lower thermal energy usage and equipment costs [31, 36-42]. Several nanoparticle-ink deposition methods (e.g. inkjetting [39, 43-45], aerosol-jet [41, 46-49], microextrusion [50-53] and roll-to-roll printing[9]) have been developed to deposit nanoparticle inks. These deposition methods are characterized by high spatial resolution, low-cost, potential scalability and ambient condition operation.

If the above desirable qualities of ink deposition techniques are to be retained within the overall manufacturing process, then the sintering method used in conjunction with the deposition should have the following characteristics:(1) low-cost and low spatial footprint; (2) ambient-condition/low-temperature sintering for compatibility with a
variety of base object materials; (3) physics-based understanding and control to achieve desired density, morphology and functionality of the sintered material; (4) wide materials capability including multi-material unary, binary, ternary and quaternary conducting and semiconducting nanoparticles. Table 1.2 compares current nanoparticle-ink sintering processes, in light of the above needs.

Table 1.2: Comparison of nanoparticle sintering processes

<table>
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<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Furnace</td>
<td>Chamber</td>
<td>$$</td>
<td>High</td>
<td>High</td>
<td>[54, 55]</td>
</tr>
<tr>
<td>P2</td>
<td>Microwave</td>
<td>Chamber</td>
<td>$$</td>
<td>Medium</td>
<td>Medium</td>
<td>[13, 56, 57]</td>
</tr>
<tr>
<td>P3</td>
<td>Laser</td>
<td>Ambient</td>
<td>$$$</td>
<td>Medium</td>
<td>High</td>
<td>[56, 58-60]</td>
</tr>
<tr>
<td>P4</td>
<td>Electrical</td>
<td>Ambient</td>
<td>$</td>
<td>Low</td>
<td>Medium</td>
<td>[1, 61-63]</td>
</tr>
<tr>
<td>P5</td>
<td>Photonic Sintering</td>
<td>Ambient</td>
<td>$$</td>
<td>Medium</td>
<td>Low</td>
<td>[8, 11, 64-68]</td>
</tr>
</tbody>
</table>

Furnace sintering (P1) is thermally intensive and costly, e.g., after microextrusion [57] the deposited nanoparticles and substrate are heated together to about 200-500°C for 1-2 hours. This places limitations on the usable substrate materials and reduces the overall throughput as well. For example, in roll-to-roll deposition combined with thermal sintering with a typical furnace sintering time of 30 minutes and roll-to-roll speed of 1 m/s, the production line is about 1.8 km long [56]. Increasing the sintering speed by raising furnace
temperature increases equipment costs drastically and causes thermal damage to the substrate. Both furnace and microwave sintering (P2) are performed inside a closed chamber, instead of under ambient conditions. Laser sintering of nanoparticles (P3) is a well-established process, but suffers from high equipment costs. Further, laser sintering can have a limited materials capability since the single wavelength of the laser may not be absorbed efficiently by a desired nanoparticle material. Electrical sintering (P4) uses induced resistive heating of the nanoparticles to cause nanoparticle densification. However, it is fundamentally limited by the fact that the nanoparticle material must be highly conductive, which is not true of many semiconductor materials used in photovoltaic cells. Furthermore, initial neck growth between the particles must be established with some thermal heating in order to establish a pathway for current to flow during resistive heating. Photonic Sintering (P5), in its current form in literature, uses pulsed xenon lamp light to sinter mostly metallic nanoparticles under ambient conditions. It is up to 100 times faster than furnace sintering, while achieving similar sintered density (Figure 1.4 [3]). Further, the broad spectrum nature of the xenon lamp light (Figure 1.5) creates the possibility that the light energy can be absorbed by a variety of nanoparticle materials.

These advantages make photonic sintering an ideal candidate for combining with nanoparticle deposition processes, for low-cost and multi-material-capable 2D and 3D additive manufacturing.
Figure 1.3: Spectral output of xenon lamp used in this work
Chapter 2: Literature Review, Challenges and Project Goals

This section describes the current literature in the area of photonic sintering and their key findings. Subsequently, the challenges in photonic sintering and the key goals of this work are discussed.

2.1 Literature review

Photonic sintering was made public in 2006 [69] by NovaCentrix, and as such it is still a very new process. Past publications on photonic sintering (also known as intense pulsed light i.e. IPL or flash light sintering due to the pulsing of the xenon lamp light) concentrate on a variety of different facets of the technology. For the purpose of this review, three main categories were identified, which are as follows:

1. Comparisons of photonic sintering to current sintering processes.

2. Materials and optimization of photonic sintering

3. Theoretical aspects of photonic sintering

2.1.1 Comparison of photonic sintering to current sintering processes

Niittynen et al. (2014) [1] performed a very thorough comparison of thermal sintering to plasma, laser, and photonic sintering. Silver ink from Harima Chemicals was deposited by inkjetting onto both polycarbonate and polyamide substrates. After deposition and sintering by the various methods, the mechanical and electrical properties of silver film deposited on polyamide were tested and compared. Thermal sintering formed a baseline to which the other processes were compared. Of the processes, thermal sintering and
photonic sintering received the highest points for both electrical and mechanical properties – photonic sintering was the only process to yield results on par with those of the thermally sintered sample. SEM of both processes are shown below in Figure 2.1a-b.

![Figure 2.1a: Thermal Sintering](image)

![Figure 2.1b: Photonic sintering](image)

The authors concluded that photonic sintering had the most potential to act as a replacement for thermal sintering in industrial applications (especially roll to roll printing).
At the same time they also noted that significant work was needed to optimize the process and achieve control of sintered material density and temperature for different material types.

Galagan et al. (2013) [3] made a direct comparison between photonic sintering and thermal sintering while focused on a specific application – photonic sintering of conductive grids for use in photovoltaic cells. Lines of 30-50 nm silver nanoparticle ink was deposited onto both glass and polyethylene naphthalate (PEN) substrates. The quality of the traces created with photonic sintering were essentially identical to those created by thermal sintering, with one difference. The grids sintered with the flashlamp had a more crisp profile with a width of 260 µm (compared to 290 µm for the thermally sintered grids) but the traces exhibited the “coffee stain” effect.

![Figure 2.2: Cross-section profile of sintered lines for thermal and photonic sintering](image)

The coffee stain effect causes the thickness at the edges of the deposition to be greater than at the center, similar to the ring created on the table when coffee spills down a mug and is trapped under the outside edge. The authors concluded that photonic sintering
holds great potential for roll-to-roll processing because traces that took 6 hours to sinter thermally can be processed by photonic sintering in under 5 seconds without any loss of collector grid functionality. Additionally, the narrower traces created by photonic sintering resulted in higher solar cell efficiency due to decreased shadowing losses.

2.1.2 Materials and process optimization

This section will be broken down into four subsections based on the nanoparticle materials that have been sintered with photonic sintering to date including copper, silver, nickel and CIGS (Copper-Indium-Gallium-Sulphide).

Copper:

While copper is a cheaper alternative to silver for printing, the formation of copper oxides on the surface of the nanoparticles, leads to lower conductivity of sintered copper films. The papers summarized in this subsection present several solutions for the reduction of the copper oxide back to the metallic phase using photonic sintering.

Kang et al. (2014) [7] investigated photonic sintering of inkjet-printed copper oxide layers on porous substrates. The porous substrate aided in wicking away most of the solvent from the copper oxide ink, which allow the particles to be sintered in a much shorter period of time. Although the mechanism of reduction has not been extensively studied and as such is not well understood, the authors speculate that it is due to photoactive polymers act as reducing agents, in a similar manner as alcohols or acid reductants. The sheets with deposited nanoparticles were exposed to one to three pulses of light. It was observed that the first pulse lowered the sheet resistance of the copper significantly, the
second pulse lowered it slightly and the third had no effect, as shown in Figures 2.3 and 2.4.

**Figure 2.3:** Sheet resistance after a sequence of light pulses

**Figure 2.4:** Densification of CuO films. (a) As deposited (b) 1 pulse (c) 2 pulses (d) 3 pulses
This indicates that after a certain amount of energy had been delivered to the nanoparticles, depositing additional energy ceases to have an effect on the film. Furthermore, subjecting the Cu layer to excessive energy per pulse caused cracking and delamination of the film from the substrate. The authors noted that this problem can be avoided by subjecting the layers to more pulses of light with a smaller pulse width.

Ryu et al. (2011) [10] conducted tests on 30nm oxide coated copper nanoparticles that had been capped with poly(N-vinylpyrrolidone) (PVP) with similar results. The authors proposed that the reduction of the oxide layer was due to a reaction with an alcoholic agent released during the decomposition of PVP. They found that the PVP capped particles resulted in full reduction of the oxide layer and subsequent sintering of the copper particles when exposed to pulses of light. The authors also found that without the polymer coating, the relative amount of copper oxide increased (relative to the particles before exposure to IPL) and the particles did not sinter well. Of the copper that was sintered, the authors found the resistivity to be three time that of bulk copper, and the film porosity to be 13.9%, as shown below in Figure 2.5.
Kim et al. (2009) [70] investigated IPL sintering of 5nm copper nanoparticles subjected to pulses of light from 30-50J/cm². They found that the higher the energy that is applied, the better the film structure of the sintered particles, and hence the better the conductivity of the copper layer, which can be seen in Figure 2.6, below. The authors also showed that even with the maximum pulse energy, the copper layer was still porous and had a resistivity of 5 µΩ·cm, approximately three times greater than that of bulk copper but about three times lesser than that of thermally sintered copper layers.
Wang et al. (2013) [6] addressed the formation of oxide layers on copper nanoparticles through the development of a copper ion ink. The ink was produced by the reaction of copper (II) hydroxide with formic and citric acid in water, to which PVP, 2-methoxyethanol and ethylene glycol were added to reduce the coffee ring effect as well as modify the viscosity for inkjetting. The deposited ink was subjected to pulses of light ranging from 16.5-80.7 J/cm². At 40.6 J/cm² the organic compounds were removed and necks were formed between the particles. Above 70.5 J/cm², bubbling of the copper layer and distortion of the PET and PI substrate was noted, with a corresponding increase in resistivity of the film. Between 40.6 and 60 J/cm², however, the resistivity was relatively constant (between 4.62 and 3.21 μΩ cm). The results are shown in Figure 2.7, below.
Lastly, the authors conducted bending tests on the printed and sintered copper electrodes and found that resistance increased for all bending radiiuses due to cracking of the copper layer, but if the bending was limited to a 20mm in diameter then the resistance leveled off slightly above 5µΩ cm after about 400 cycles (Figure 2.8).
Dharmadasa, et al. (2013) [5] created a copper ink through chemical synthesis of Cu/Cu2O nanoparticles. While similar effects of IPL process parameters as above were seen by the authors, a key observation was the effect of the size of nanoparticle inks. Inks with nanoparticle sizes of 10-15nm and 100-120nm were examined in terms of the sheet resistance of the sintered material. The sheet resistance was found to reduce with a reduction in nanoparticle size. The hypothesis forwarded by the authors was that smaller nanoparticles have lower melting points and thus require lesser energy to melt. However, the microstructures of sintered material with smaller and larger nanoparticles were not compared. Further, SEM images showed interparticle neck growth but not significant melting (Figure 2.9).
Silver:

Of the all the materials used in photonic sintering, silver has many advantages. It does not form oxides when exposed to air, it has a relatively low melting point, and it is also one of the cheaper noble metals available.

Hosel et al. (2012) [9] focused on photonic sintering of silver for use in roll-to-roll processes combined with photonic sintering. They successfully sintered two silver inks with a low energy density (1.75 J/cm²) single pulse of light. As in the case of copper, they observed that increasing energy density resulting in improved density of the sintered material and reduced sheet resistance (see Figure 2.10).
However, the authors also noted that at high energy densities, cracks were formed in the silver layer. These cracks were probably formed due to excessive stresses in the material during sintering. So balancing densification with prevention of temperature and stress gradients is a challenge still needing to be overcome.

Lee et al. (2011) [107] sintered an ink composed of 5-7nm diameter nanoparticles, suspended in tetradecane at 57% by weight, with a single pulse of light ranging from 5-30 J/cm$^2$. The nanoparticle film began to sinter at 10 J/cm$^2$, but also delaminated and swelled up slightly. At 20 J/cm$^2$, the film swelled and ruptured, but at 30 J/cm$^2$ the swelling/rupturing disappeared. The authors concluded that the localized surface deformation is due to rapid flashing of the organic additives underneath the sintered top layer of silver. As shown in Figure 2.11 below, the authors also showed the same trend in resistance of the sintered materials with respect to light energy density - increasing the
energy density up to 15 J/cm² results in decreasing resistance, while increasing the energy density further has no effect.

Figure 2.11: Resistance vs. Light energy

In a subsequent publication, Park et al. (2013) [4] addressed the surface deformation problem of the previous study by introducing a two-step photonic sintering process. In the two-step process, a silver ink (57.2 wt%, 8-15nm in tetradecane) was exposed to a low energy preheating flash of light followed by a higher energy main sintering pulse. It was found that by tuning the preheating pulse to 10 J/cm² and the main sintering pulse to 20 J/cm² resulted in a film with even sintering, no delamination from the substrate, and a low resistivity of 36.32 nΩ m which is below the value of 40.84 nΩ m for the same ink that was thermally sintered. This optimal film produced by IPL sintering is shown in Figure 2.12, below.
Chung et al. (2013) [108] developed a method to monitor sheet resistance of the silver film in situ by using the printed silver as one leg of a Wheatstone bridge and measuring the voltage across the bridge with an oscilloscope, as seen in Figure 2.13.

The authors optimized the energy deposition as well as the pulse length and frequency to provide good densification without damage to the PET substrate. Through the in-situ monitoring method, they found that each pulse of light decreased the sheet resistance of
the silver lines until it settled at 6.5 Ω/sq. after the third pulse. Substrate damage started at the fourth pulse. Interparticle necking was also found to increase with increased energy deposition, as in other studies. SEM images of the densification of the silver nanoparticles after various numbers of pulses are shown in Figure 2.14.

![Figure 2.14: Silver densification](image)

Figure 2.14 shows the plot generated by the oscilloscope during the 10 pulse case.

![Figure 2.15: Sheet resistance vs. time plot for the 10 pulse sample](image)
The first four pulses can be clearly seen in the above figure, but after the 4th pulse, no significant effect of flashing on the sheet resistance of the silver film can be seen. The reason for this phenomenon was not investigated in this study or in other studies. As will be shown in this work (Chapter 4) part of the reason behind this is that photonic sintering is an inherently self-damping process.

Nickel:

Park et al. (2014) investigated photonic sintering of two different nickel nanoparticle inks [8], one with a fairly uniform particle diameter of 50nm, and the other with particles ranging from 5-500nm. The goal of the research was to investigate the effects of different particle sizes on the quality of the sintered material. The light energy and pulse pattern was varied to find the optimal sintering parameters. A two stage process was utilized, in which the inks were preheated by a series of lower energy flashes (7.5-12.5 J/cm²), and then sintered in a second stage with a higher energy density (7.5-17.5 J/cm²). At these energy levels, only the ink with 5-500nm particle distribution could be sintered. The authors indicated, similar to the others that dealt with sintering silver and copper, that higher energy levels were advantageous for sintered film quality. The results of these tests are shown in Figures 2.16-2.17, below.
Since the 50 nm nickel ink (labeled QNI in Figure 2.16) did not sinter well in their tests, (see Figure 2.16 for resistivity measurements of both types of ink) the authors concluded that the ink with a wider particle distribution sinters with greater final density. However, they did not test any inks with small nanoparticles and a narrow distribution of particle size – the greater density of the sintered films may be due to the greater melting of small particles rather than the wide distribution of particle sizes. They hypothesized that this was due to the wide range of plasmon resonance of differently sized particles resulting in
better absorption across the broad spectrum of incident light, in conjunction with the ability of the particles of a diameter less than 10nm to fill in the gaps between larger particles and quickly melt to join the larger surrounding particles (due to their depressed melting point). However, there was no effort to theoretically model and verify this particle melting based hypothesis especially considering the fact that nanoparticle ensembles absorb light very differently than individual nanoparticles. The possibility of interparticle necking was also not accounted for. No attempt was made to understand what ratios of nanoparticle sizes, in what ratios by weight or volume, result in what kind of densification or temperature rise (of nanoparticles or substrate) during sintering.

Figure 2.17: FIB cross-section of (a) dried film (b) sintered film using a 7.5 J/cm² preheat and a 17.5 J/cm² sintering pulse

CIGS:

Dhage et al. (2011) [2] addressed synthesis of CIGS from Cu(In,Ga) (CIG) and Se nanoparticles in order to overcome environmental and potential human health problems
associated with conventional CIGS manufacturing. The nanoparticles were deposited on the surface in a 1:1 molar ratio \( \text{Se}_2 : \text{Cu(In}_{0.7}\text{Ga}_{0.3}) \) in order to form the desired \( \text{Cu(In}_{0.7}\text{Ga}_{0.3})\text{Se}_2 \) compound. The deposited particles were then subjected to pulsed light varying from 5-20 J/cm\(^2\). Although CIGS was synthesized at energies as low as 5 J/cm\(^2\), the amounts of unreacted precursors were found to be lowest (almost negligible) at the highest light energy (50 J/cm\(^2\)). The advantage of using photonic sintering was a fast processing time and an environmentally less hazardous process (no selenization). However, trace amounts of unreacted CIG rendered the photoactivity of the absorber low.

Table 4 below summarizes the key observations from the above literature, on the effects of critical process parameters on densification and temperature during photonic sintering:
<table>
<thead>
<tr>
<th>Increase in</th>
<th>Effect on density</th>
<th>Effect on temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power per pulse</td>
<td>Increasing density with increasing power levels per pulse.</td>
<td>Not directly investigated, substrate damage increased with increasing power, suggesting higher temperatures were reached with higher power levels</td>
</tr>
<tr>
<td>Pulse timing</td>
<td>• Increased density with increasing pulse duration.</td>
<td>Not investigated</td>
</tr>
<tr>
<td></td>
<td>• Increased density with decreased off time between pulses.</td>
<td></td>
</tr>
<tr>
<td>No. of pulses</td>
<td>• Increase in density with increasing number of pulses.</td>
<td>Not investigated</td>
</tr>
<tr>
<td></td>
<td>• However, beyond a certain number of pulses there is no increase in density.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No physical explanation for this was provided.</td>
<td></td>
</tr>
<tr>
<td>Particle size</td>
<td>• The presence of even a very small fraction of small particles (&lt;10nm) result in higher density.</td>
<td>Not investigated</td>
</tr>
<tr>
<td></td>
<td>• No results reported on the relative effect of mixing different nanoparticle sizes in different percentages by weight.</td>
<td></td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>Not investigated</td>
<td>Not investigated</td>
</tr>
</tbody>
</table>
Table 2.1 shows that there have been very few experimental or theoretical attempts to link densification and temperature evolution in photonic sintering to nanoparticle sizes in the ink. Furthermore, there have been no attempts till date to combine photonic sintering and nanoparticle ink deposition into a low-cost, desktop additive manufacturing system.

2.1.3 Theoretical modeling of photonic sintering

West, et al. (2012) [69], compared experimental sintering results to a model developed by the authors. This model approximates light absorption with the Bruggeman effective medium theory and then predicts the depth of sintering into the film due to heat transfer from the heated surface, using the commercial heat transfer simulation package Fluent. The model calculates the amount of energy that will be absorbed by the nanoparticles using a modified Bruggeman model, (modified by the authors with the extended Drude model to provide a model that more closely matches the absorption curve of 5 and 15nm silver nanoparticles found experimentally). Although the details of these modifications were not presented, the standard Bruggeman dielectric function is given in the text as follows:

\[
f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon} = 0
\]

\[\text{..................(2.1)}\]

Where \(\varepsilon\) is the dielectric function of the effective medium, \(\varepsilon_a\) is the dielectric function of the particles in the medium, \(\varepsilon_b\) is the dielectric function of the medium, \(f_a\) is the volume fraction of the particles contained in the medium, and \(f_b\) is the volume fraction of the particles contained in the medium. Once the average dielectric function is found, the imaginary portion of the refractive index and the absorption coefficient for the effective medium can be calculated by the expression:
\[ \alpha' = \frac{4\pi k}{\lambda} \quad (2.2) \]

Where \( k \) is the imaginary part of the refractive index and \( \lambda \) is the wavelength of light. From this, using the Beer-Lambert law, the absorption spectra can be calculated.

Using the modified model (of which the equations are not given in the text), the authors arrive at the plot shown in Figure 2.18. The amount of energy absorbed into the deposited silver nanoparticles was then used as an input to a Fluent heat transfer model to calculate the temperature rise of the material. Using the fluent simulation, the authors calculated the temperature in the film as well as the liquid volume fraction at three depths throughout the 900\( \mu \)s lamp pulse.

![Figure 2.18: Theoretical and experimental absorption curves](image)

The experimental portion of the research again indicated that higher energy densities results in better sintering, but above a certain energy density the silver film was damaged by cracking and delamination. In this case, the density of the silver deposition was
calculated by weighing the glass slide before and after the particles are deposited in a 3mmx10mm pad to determine the mass of particles deposited. The thickness of the deposition was measured using a Zeiss Imager M1M microscope. The volume of the particles was then found using the following equation:

\[ V = l \times w \times t \] ........................................(2.3)

*Where:*

\[ l = length \]

\[ w = width \]

\[ t = thickness \]

Experimental testing indicated that a 24.6µm thickness of nanoparticles densified to a thickness of 11µm upon exposure to the pulsed light. Using the above method, the maximum density measured was 83.87% that of bulk silver. Another test performed was to deposit three films 1.0, 3.1 and 5µm thick and placing them in a spectrophotometer to measure the light absorption of the films of light ranging in wavelength from 190 to 820nm. The results are shown in Figure 2.18.
This indicated that any sintering effects beyond 5µm into the deposited silver film were primarily driven by conduction of heat from the top layer. Since the film was sintered to a depth of 24.6µm, a significant portion of the sintering was driven by heat conduction into the particles below the depth to which light can penetrate.

While this kind of mesoscale model gives a good indication of how heat transfer influences the temperature evolution of the deposited nanoparticle ensemble, it does not provide much insight into what is happening at the particle level during photonic sintering. For example, the likelihood that there is significant neck growth between the particles before the melting point is reached is not considered. Furthermore, the heat generation is based upon light absorption of the as-deposited nanoparticles and thus any possible effect of the above neck growth on the light absorption by the nanoparticle ensemble is ignored.

Kim et al. (2009) [70] experimentally quantified light absorption by the deposited nanoparticles, and combined it with known nanoparticle mass to predict nanoparticle
melting. Again, any possibility of neck growth and a dependence of light absorption on neck growth was ignored. Outside the field of photonic sintering, multiple models exist to quantify optically-induced heating and heat transfer in nanoparticles [71-76]. However, these models do not capture densification and its effects on light absorption in nanoparticle ensembles. Past models of mass transport during nanoparticle and micropowder sintering [62,77,78] do not include light absorption. However, these theoretical efforts do yield the following relevant information:

1. Larger nanoparticles generate more heat than smaller nanoparticles. Further, the amount of heat generated depends significantly on the number of nanoparticles. This is relevant in trying to understand the effect of particle size on temperature and density evolution in photonic sintering.

2. Optically-induced heat generation by nanoparticles depends significantly on the shape of the nanoparticles as well. If solid-state necking occurs between the nanoparticles during photonic sintering, then this is expected to change both the size and the shape of the nanoparticles, and therefore the heat generation as well.

3. Neck growth between nanoparticles is governed by both bulk and surface diffusion. Under the same temperature rise, neck growth will be faster in smaller nanoparticles than in larger nanoparticles of the same material.

4. The melting point of nanoparticles can be significantly lower than that of the corresponding bulk material.

The above phenomena and the assumptions made in current modeling methods indicate that a consideration of nanoscale phenomena, beyond just the depression in melting
point is needed in order to improve our understanding of the photonic sintering process. Furthermore, since the goal of the current photonic sintering models is to predict melting and not just densification, these models might be over predicting the pulse energy required to achieve densification. Practically speaking, this would result in a higher temperature rise than is required.

The above state-of-the-art models relevant to photonic sintering are described in greater detail in chapter 4, which deals with nanoscale modeling of photonic sintering. As will also be seen in chapter 4, fundamental models of optical absorption by nanoparticles indicate that optically-induced heating of the nanoparticles cause both a temperature rise and a solid-state neck growth between the nanoparticles. However, a key difference between light-induced heating of micro and nanoparticles is that this neck growth in the case of nanoparticles significantly reduces the heat generated in the nanoparticles. The absence of this physics in the above models creates a significant drawback.

2.2 Challenges

The key challenges that can be identified from the above literature review include

1. Quantification of temperature evolution during sintering, specifically for different particle size mixtures, and correlation of the nanoparticle sizes to the densification and temperature in photonic sintering.

2. Nanoscale understanding of the photonic sintering process, in terms of possible interparticle neck growth before melting and its effect on optical heat absorption by the nanoparticle ensemble.
3. Development of a low-cost additive manufacturing prototype that combines photonic sintering and nanoparticle inkjet deposition, towards low-cost and multi-material capable additive manufacturing of non-polymeric materials. Within the authors knowledge no such system exists today.

2.3 Goals:

The goals of the present work are to:

1. Experimentally characterize densification and temperature evolution in photonic sintering as a function of nanoparticle size and material type (elemental metallic vs. non-metallic compounds)

2. Computationally model and understand the nanoscale physics behind photonic sintering, use this model to qualitatively explain observed experimental trends and to examine whether current photonic sintering models adequately describe the process physics.


The following chapters describe the tasks that were performed to achieve the above goals, and the corresponding results were observed.
Chapter 3: Effect of Particle Sizes and Nanoparticle Material on Densification and Temperature Rise

3.1 Experimental setup

Initially, sintering tests were performed using a static test setup (Figure 3.1) in which nanoparticle inks were deposited onto strips of mirror finish 304 stainless using a micropipette. A continuous xenon-lamp light source, PerkinElmer 300, was used as the light source with the output directed to the sample through a 3.5mm bundle diameter fiber optic light guide. This light source is capable of outputting a maximum of 300W of optical power with a spectrum shown in Figure 1.5. In addition a Micro Epsilon thermolIMAGER TIM 200 was used to monitor temperature evolution of the deposited nanoparticles and of the substrate during sintering. The TIM 200 simultaneously records visual image and an IR video. The visual camera has a 32Hz frame rate and a resolution of 640x480, while the thermal imager records at 128Hz with a resolution of 160x120. In the static setup, the TIM 200 gave a resolution of 96 pixels per inch. The thermal imager can measure temperatures of -20°C to 1500°C (over 4 measurement ranges) with an accuracy of +/- 2% or +/- 2°C.

The following sections describe densification of nanoparticles as well as the temperature evolution, for the nanoparticles and the substrate, in these static tests. These results are first described for silver nanoparticles of different diameters. Note that our focus was on the effect of particle sizes because the effect of photonic sintering power and time is already well known from literature (see Chapter 2). This is followed by the results
obtained for sintering of other nanoparticles including ITO (Indium Tin Oxide), AZO (Aluminum Zinc Oxide) and WC (Tungsten Carbide).

Figure 3.1: Static test setup

3.1 Effect of particle size on densification

To investigate the effect of nanoparticle size on densification we choose the following three silver nanoparticle inks, i.e., (1) 10nm diameter silver in tetradecane (50% by weight), (2) 20nm diameter silver, 50 wt% in tetradecane, (3) 40nm diameter silver, 50 wt% in tetradecane. The inks were obtained from Sigma Aldrich (10nm) or mixed from particles obtained from US-Nano (20/40nm). 1µl of each of the inks were deposited and exposed to the full lamp power for 10 seconds. The sintered material was analyzed using the Quanta 3D dual beam Scanning Electron Microscope (SEM) in the Oregon State
microscopy center. Figure 3.1a shows the layer of silver sintering with 10 nm inks. Cross-sectional images of the film obtained after Focused Ion Beam machining are shown in Figure 3.2b. Note that the lumps seen in Figure 3.1a are probably nanoparticle agglomerates formed due to poor mixing in the ink, even before sintering. One of these lumps is shown in Figure 3.2c. Figures 3.3 and 3.4 show SEM images of sintered silver for 20 nm and 40 nm diameter silver inks. Even without a cross-sectional image for the 20 nm and 40 nm inks it is clear that densification with these larger nanoparticle diameters is much poorer than for the 10 nm diameter nanoparticles.
Figure 3.2: SEM images of sintered material for 10nm diameter silver ink

Figure 3.3: SEM images of sintered material for 20nm diameter silver ink
Figure 3.4: SEM images of sintered material for 40nm diameter silver ink

We further investigated the effect of mixing silver nanoparticles of different diameters on the densification. The nanoparticles were mixed to create total 50% by weight of silver nanoparticles in the ink. The specific ratios in which the nanoparticles were mixed are shown in Table 3.1. Figures 3.5-3.8 show the SEM images of sintered material when inks with different mixing ratios for 10 nm and 20 nm diameter nanoparticles were used.
<table>
<thead>
<tr>
<th>Particle sizes that were mixed</th>
<th>Mixing ratio (ratio shown is that of smaller to larger diameter nanoparticles by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm &amp; 20 nm diameter</td>
<td>1:4</td>
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<tr>
<td></td>
<td>2:3</td>
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<td>10 nm &amp; 40 nm diameter</td>
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<td></td>
<td>4:1</td>
</tr>
</tbody>
</table>

It can be seen (by comparing Figure 3.5 to Figs. 3.3 and 3.4) that necking between the particles may be slightly improved by mixing the nanoparticles as compared to using pure nanoparticles. However, the density for the 1:4 ratio (Figure 3.5) is not as high as that for pure 10 nm nanoparticles. At the same time, increasing the mixing ratio (Figs. 3.6-3.8) seems to create secondary sintered structures between the larger nanoparticles, which fills the pores and results in enhanced densification. Figure 3.9 shows a cross-sectional image of sintered material for the case of the 4:1 mixing ratio which shows larger nanoparticles embedded within a solid and dense matrix. Contrasted to the case of pure 10 nm nanoparticle ink (Figure 3.2b), Figure 3.9 shows the presence of more pores in the sintered material. Further, as compared to the pure 10 nm ink the presence of the larger nanoparticles in the mixed ink significantly degrades the surface finish of the sintered film.
Similar effects are seen in Figs. 3.10-3.13 for the case of mixing 10 nm and 40 nm diameter inks. The implications and possible questions raised by this phenomena will be discussed in the summary section of this chapter.

Figure 3.5: SEM images for sintered Ag 10nm and 20nm nanoparticles mixed in the ratio 1:4 by weight
Figure 3.6: SEM images for sintered Ag 10nm and 20nm nanoparticles mixed in the ratio 2:3 by weight
Figure 3.7: SEM images for sintered Ag 10nm and 20nm nanoparticles mixed in the ratio 3:2 by weight
Figure 3.8: SEM images for sintered Ag 10nm and 20nm nanoparticles mixed in the ratio 4:1 by weight
Figure 3.9: Cross sectional SEM image of sintered silver nanoparticles for Ag 10nm and 20nm nanoparticles mixed in the ratio 4:1 by weight
Figure 3.10: SEM images for sintered Ag 10nm and 40nm nanoparticles mixed in the ratio 1:4 by weight
Figure 3.11: SEM images for sintered Ag 10nm and 40nm nanoparticles mixed in the ratio 2:3 by weight
Figure 3.12: SEM images for sintered Ag 10nm and 40nm nanoparticles mixed in the ratio 3:2 by weight
Figure 3.13: SEM images for sintered Ag 10nm and 40nm nanoparticles mixed in the ratio 4:1 by weight
3.2 Effect of particle size on temperature evolution

The thermal camera shown in Figure 3.1 was used to measure temperature of the deposited nanomaterials and of the substrate during photonic sintering. First, the camera was calibrated for the stainless steel substrate using the following method (1) Heat stainless to 100°C, as indicated by the thermistor, on a hot plate; (2) Adjust the emissivity to have the surface show a temperature of 100°C. The emissivity of the stainless steel substrate was obtained as 0.182, as compared to the typical value of 0.075 used in literature. Each ink was brushed onto the same piece of stainless steel, and calibrated in the same manner to obtain the emissivity of the deposited material. Figure 3.14 shows infrared images of the substrate and of the deposited nanomaterial during the calibration process for some of the inks considered in the previous section.

![Figure 3.14: Infrared image with peak temperature during calibration of emissivity of (a) substrate (b) 10 nm diameter Ag ink (c) 20 nm diameter Ag Ink (d) 40 nm diameter Ag ink](image)

Note that no temperature rise was recorded by the camera when the nanoparticles were deposited without the light turned on, or when the light was turned on without any nanoparticles deposited. This shows that the small amount of near-IR radiation in the lamp's spectrum has a negligible effect on the temperature recorded by the camera.
Figure 3.15: (a) Temporal evolution of the peak temperature during sintering of Ag nanoparticles without any mixing (b) Spatial temperature profile on the plane of the substrate during sintering, when peak nanoparticle temperature is reached.
Figure 3.15 shows the effect of nanoparticle size on the temperature during sintering, when no nanoparticle mixing is performed. As far as the deposited nanomaterial is concerned (Figure 3.15a), there is a sharp increase in the temperature when the xenon lamp is switched on, followed by stabilization to a steady value. More importantly, the peak temperature and the steady-state temperature are much higher for sintering of larger nanoparticles than for sintering of smaller nanoparticles. The temperature rise of the substrate (Figure 3.15b), around the deposited nanoparticles, is greater for the smaller nanoparticles than for the larger nanoparticles. For example, for 20 nm and 40 nm inks the temperature is confined primarily within the spot of the xenon lamp light.

Note that in Figure 3.15b the temperature reading is cut off above 275 degrees Celsius. This is because the thermal camera reads within four distinct manually set temperature ranges. Since measurement of substrate temperature was the goal the camera was used in the range of 25-275 degrees Celsius and fusion of temperature data with a reading from a lower temperature range was not performed. Therefore, the temperature above 275 degrees was not captured. Figure 3.16 below shows the temporal evolution of the peak temperature of the deposited nanoparticles during sintering, when 10 nm and 20 nm nanoparticles are mixed (Table 3.1).
Figure 3.16: (a) Temporal evolution of the peak temperature during sintering of mixed 10 nm and 20 nm Ag nanoparticles, with mixing in the ratios shown in Table 3.1.
Three key inferences can be made from the above, namely (1) Mixing of the nanoparticles results in peak and steady state temperature that are in between corresponding values for sintering of corresponding unmixed nanoparticles; (2) Changing the ratio of the nanoparticles by weight does not have a significant influence on the peak and steady state temperature during sintering; (3) Changing the diameter of the larger nanoparticle also does not seem to affect the sintering temperatures significantly.

Figure 3.17 shows the spatial temperature profile in the plane of the substrate, for the cases shown in Figure 3.16. Note that an increase in the ratio of 10 nm nanoparticles leads to significantly greater temperatures outside the spot diameter of the xenon lamp light. For example Figure 3.17a shows that the temperature at around 2.5 mm from the center of the deposited nanomaterials (10 nm and 20 nm mixed) is about 40°C for mixing ratio 1:4 and is about 100°C for mixing ratio 4:1. A similar effect is observed for mixing of 10 nm and 40 nm nanoparticles (Figure 3.17b).
Figure 3.17: Spatial temperature profile on the plane of the substrate during sintering, when the peak temperature of the nanoparticles is reached for mixtures of (a) 10 nm and 20 nm Ag nanoparticles and (b) 10 nm and 40 nm Ag nanoparticles.
3.3 Sintering of non-elemental nanoparticles

Preliminary experiments were also performed to explore the ability of photonic sintering to sinter non-metallic materials. The results of these experiments are described briefly in this subsection. The nanoparticle materials chosen were 55nm diameter Tungsten Carbide (WC) suspended in Tetradecane in 50% by weight, 15nm Aluminum Zinc Oxide (AZO) nanoparticles suspended in water in 15% by weight and 20-70nm Indium-Tin-Oxide (ITO) nanoparticles suspended in water in 33% by weight. Figures 3.18-3.20 show SEM images of the sintered nanoparticles. Solid state necking between the nanoparticles can be observed for all three materials, with WC exhibiting the greatest degree of necking of the three (Figure 3.18).

Figure 3.18: SEM images of sintered WC nanoparticles
The evolution of nanomaterial temperature for all three of the above nanomaterials (Figure 3.21) shows that the temperature rise is highest for WC and is the lowest for AZO. In fact, the temperature rise for WC is so high that it goes beyond the maximum measurement temperature of the camera (1500°C). The higher temperature rise might...
be the reason why greater interparticle necking is seen in WC as compared to the other two materials. Figure 3.22 shows the spatial profile of the substrate temperature at peak nanoparticle temperature for all three nanomaterials. As expected, the rise in substrate temperature outside the xenon light spot is much higher for WC than it is for ITO and AZO.

Figure 3.20: SEM images of sintered AZO nanoparticles
Figure 3.21: Evolution of nanoparticle temperature during sintering of WC, ITO and AZO.

Figure 3.22: Spatial temperature profile on the plane of the substrate during sintering, when the peak temperature of the nanoparticles is reached for sintering of WC, ITO and AZO.
3.4 Summary

The above experimental results show some interesting phenomenon which are now summarized along with some of the fundamental questions that these observations raise.

1.) The sintering experiments for silver nanoparticles show that smaller nanoparticles undergo greater densification than larger nanoparticles of the same material, under the same incident power and in the same time. At the same time, the temperature rise in smaller nanoparticles is lower. The lower temperature rise can be easily explained by the well-known fact that larger nanoparticles generate much more heat (orders of magnitude higher) than smaller nanoparticles. However, the question that still remains to be answered is why is densification in smaller nanoparticles greater despite a significantly lower temperature rise? One commonly used answer is that particle melting occurs due to lower melting point of smaller nanoparticles. Given the temperatures seen in Figs. 3.15 and 3.16, which are much lower than the melting points of silver, how far is the above explanation valid? Further, note that the curvature effects that cause reduced melting points in nanoparticles can be lost if interparticle neck growth occurs.

2.) A common assumption made by existing models of photonic sintering is that the amount of photonic heating of the nanoparticles is constant through the sintering process. If so, then why is there a spike and then a stabilization of temperature in Figs. 3.15 and 3.16? One answer to the above is that radiation to the environment and conduction to the substrate results in a steady state temperature being
reached. To what extent does this explanation capture the physics of the photonic sintering process?

3.) When using mixed nanoparticle inks, it is observed that the larger nanoparticles seem to be embedded in a matrix of dense material. However, the occurrence or absence of this phenomena depends on the ratio of number of smaller to larger nanoparticles. Further the temperature rise of the mixed inks during sintering falls between that of the pure nanoparticle inks – higher than the pure smaller nanoparticle ink and lower than the pure larger nanoparticle ink. Why is the above dependence on the mixing ratio observed?

4.) Mixing of different sized nanoparticles also results in reduction of surface finish quality. However it is not clear how fast densification occurs in a mixed nanoparticle inks as compared to pure nanoparticle inks. Also, does the speed of densification in a mixed nanoparticle ink depend on the relative ratio of smaller to larger nanoparticles by weight?

5.) Non-metallic nanoparticles can also be sintered using photonic sintering. The different degrees of optical response of different materials, to the spectrum of xenon lamp light, will result in different sintering and substrate temperatures as well as different degrees of densification. How can the degree of densification in photonic sintering of different nanomaterials be predicted?
The answers to some of the questions raised above can be found via the multiphysical model described in the next chapter, which combine the fields of photonics and sintering to obtain a better understanding of the photonic sintering process.
Chapter 4: Nanoscale Modeling of Photonic Sintering

This chapter describes nanoscale models developed in this work to understand the link between particle size, densification and temperature rise in photonic sintering. Past efforts in modeling photonic sintering are described first, along with the key goals of this modeling effort that distinguish it from past work. This is followed by a description of the method used to implicitly couple models of photonic heating of nanoparticle ensembles with temperature rise and neck growth between adjacent nanoparticles, for both mixed and unmixed nanoparticles. Additionally, the results are compared to those that would arise from the assumptions made in current models (from literature) of photonic sintering. Then, the results from the developed model and the resulting inferences are described, in terms of the new knowledge created in understanding the underlying physics of photonic sintering.

4.1 Past Modeling Efforts and Goals of this Effort

Past theoretical work in areas related to photonic sintering are first summarized, to provide context for the subsequent discussion.

T1: When two touching nanoparticles are heated, then with time interparticle neck growth and densification occur. As the temperature rises, melting might occur as well. Analytical models and Molecular Dynamics methods have been used to predict nanoparticle densification [73, 79-83]. Further, it has been shown that neck growth between nanoparticles is governed by both bulk and surface diffusion [77, 78, 80, 82, 84-]
88]. However, to capture densification in photonic sintering, these models need input from photonic heating models.

**T2**: Multiple models exist to quantify photonic heating and heat transfer in nanoparticles [82, 88-97]. However, these models do not couple densification with photonic heating. Since the shape and size of nanoparticles changes during neck growth and both shape and size significantly influence light-induced heating [71-76], it is necessary to couple the evolution of necking to temperature and density evolution in photonic sintering.

Models developed for photonic sintering in literature, are summarized below:

**T3**: A mesoscale model of pulsed photonic sintering was developed by the Hahn group [10, 70]. They experimentally obtained the plasmonic wavelength $\lambda_p$ of as-deposited Cu nanoparticles and obtained the energy absorbed by a deposited film of Cu nanoparticles ($q_0$) as in Eqn. 4.1 below.

$$q_0 = (\text{Optical Absorption at } \lambda_p) \cdot E_{\text{lamp}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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the Cu nanoparticles was obtained based on size effects, after another paper by the same authors [70]. Further, the rise in temperature of the substrate was also predicted.

**T4: West et al. [72] developed a similar mesoscale model for photonic sintering. The absorption spectrum of a layer of as-deposited Ag nanoparticles was obtained experimentally. An effective medium theory along the lines of the Bruggeman Dielectric function (Eqn. 4.2) was used to model light absorption by the as-deposited nanoparticle film.**

\[
f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon} \text{ ..................(4.2)}
\]

Where \( f_a, f_b \): volume fractions of particles and volume fraction of the medium respectively; 
\( \varepsilon_a, \varepsilon_b \): dielectric function of the particles and the medium; \( \varepsilon \): effective dielectric function

This model for heat absorption was used with conventional heat transfer models in FLUENT to model temperature evolution in the silver nanoparticle film and on the substrate.

While the above models are able to provide an approximate mesoscale analysis of the process, they are based on certain assumptions about nanoscale phenomena, which result in the following drawbacks:

(1) Densification is not explicitly coupled to photonic heating in the above models. This has the following implications:
(a) It is expected that there will be some interparticle neck growth before melting occurs. This will change the nanoparticle size and shape (T2 above), and therefore change the amount of heat absorbed by the nanoparticles. This fundamental nanoscale physics is not examined or accounted for by the above models.

(b) The goal of the models is to predict melting, and not to control densification. Note that densification can be high even without melting of the nanoparticles. However, the lack of modeling of density evolution does not allow this factor to be accounted for. Further, note that sintered nanoparticles with controlled porosity have applications in many areas including low-k dielectrics for electronics packaging and sensing elements for gas sensors. Thus there is a need to be able to control the sintered nanomaterial density. Uncoupling densification and photonic heating loses not just an understanding of the process, but also the ability to control the process.

(2) The xenon lamp light has a broad spectrum and is absorbed by the nanoparticles over this spectrum by variable amounts. The total energy absorbed is a sum of the energy absorbed at each wavelength integrated over the power spectrum of the incident light. Assuming that energy is absorbed only at the plasmon resonance wavelength, as in the above model, can underestimate the heat generated and temperature rise in the nanoparticles. This can lead to excessive heat generation in the nanoparticles and underestimation of the temperature rise of the underlying substrate.

To summarize, models of photonic sintering should include the implicit coupling between plasmon resonance, heat generation and densification in order to capture the nanoscale
physics in the process and thus to control the process. The goals of this modeling effort are to (1) create the above multiphysical coupling in order to investigate the above nanoscale effects in photonic sintering; (2) examine if the developed model reflects experimental trends seen in Chapter 3; and (3) examine if the current mesoscale models for the process (T3 and T4) are able to capture the observed experimental trends in photonic sintering. The next few sections describe the model developed in this work and predictions for Ag nanoparticles.

4.2 Unmixed Nanoparticles

This subsection describes the sintering model, photonic heating model, the coupling between them and the model predictions for unmixed nanoparticles. Subsection 4.3 describes the extension of these models to the case of mixed nanoparticles.

4.2.1 Sintering Model

The spatial domain of our analysis is a system of five in-plane nanoparticles, of same or different sizes which are initially touching each other (examples shown in Figure 4.2a). The purpose of the sintering model is to predict the change in shape and size of this assembly due to temperature induced neck growth between the nanoparticles. In particular, we want to capture the kinematics of the densification in order to understand why smaller nanoparticles sinter to a greater density despite lower photonic heating. For the above purpose we extend a McMeeking-Cocks model [88] for sintering and coarsening of rows of particles, to account for a continuous change in temperature. In this model, the
geometry of the interface between two touching nanoparticles is described by the geometric parameters shown in Figure 4.2b. Here 2x is the neck size at any instant of time.
Figure 4.2: Schematic of model with (a) five nanoparticles of the same size touching each other before neck growth (b) five nanoparticles of different sizes touching each other before neck growth (c) geometric parameters describing the interface between two nanoparticles during neck growth. Note that in (a) and (b) the unit vectors $E$ and $k$ denote the direction of polarization and the direction of travel of the incident light respectively.

The goal is to obtain the evolution of the geometric parameters, i.e., $a, b, x, L, h$ in Figure 4.2(c), at each interface of the aforementioned system by extremizing the functional

$$\Pi = \dot{G}_s + R_s \quad \text{........................(4.3)}$$

where $G_s$ is the free energy of the system and $R_s$ is one half the rate of energy dissipation in the system.
When the temperature of a row of nanoparticles is raised, atoms travel along the free surface (surface diffusion) and also through the interparticle contacts (grain boundary diffusion) to reduce the free energy of the surfaces and interfaces of the system. This travel of atoms into the interparticle region results in a neck. Motion of these atoms requires certain amount of energy to be supplied to move the atoms over barriers to energy motion. The above functional represents the energy balance that exists between energy supplied in the form of external heat and the work done to move atoms into the interparticle neck. The stable geometric configurations are the combinations of the geometric parameters that extremize the above functional. The functional in Eqn. 4.3 can be minimized by using Rayleigh-Ritz minimization, i.e., by setting

\[ \Delta \Pi = \Delta \dot{G}_s + \Delta R_s = 0 \] ..................................(4.4)

where the \( \Delta \) denotes a small perturbation in the corresponding variable. The \( \Delta \Pi \) must be zero for arbitrary perturbations of the geometric parameters \( a, b, L, h \) and \( x \). Thus, by expressing \( \Delta G_s \) and \( \Delta R_s \) in terms of the geometric parameters and setting the coefficients of perturbations in the geometric parameters to be zero, one can derive coupled linear equations to solve for the geometric parameters. The \( R_s \) terms on the right hand side of Eqn. 4.3 are expressed as shown below.

\[ R_s = \frac{1}{2} \int_{A_b} \frac{1}{d_b} j_b \cdot j_b dA_b + \frac{1}{2} \int_{A_s} \frac{1}{d_s} j_s \cdot j_s dA_s \] ...........(4.5)

where \( A_b, A_s \)= areas of the grain boundary and the surface respectively
\( j_b, j_s \)= material flux on the grain boundary and the surface respectively
The parameters $d_b$ and $d_s$ in Eqn. 4.5 are diffusion parameters that are given by:

\[ d_b = \frac{\delta_b D_b \Omega}{kT}; d_s = \frac{\delta_s D_s \Omega}{kT} \] .................(4.6a)

where $\delta_b$, $\delta_s$= thickness of material diffusion on grain boundary and the surface respectively

$D_b$, $D_s$= grain boundary and surface atom diffusivities respectively

$k$=Boltzmann’s constant; $T$= temperature in Kelvin

Further, the diffusivities are assumed to be equal here and are modeled as functions of temperature via the Arrhenius equation

\[ D_b = D_s = D_0 e^{-E_a/(kT)} \] .................(4.6b)

where $D_0$ is the pre-exponential factor for a given diffusion mode

$E_a$ is the activation energy for diffusion

By further assuming that $\delta_b=\delta_s$, this model assumes that $d_b=d_s$. The perturbation of $R_s$, i.e. $\Delta R_s$ is expressed as in Eqn. 4.7 below:

\[ \Delta R_s = \frac{1}{2} \int_{A_b} \frac{1}{d_b} \mathbf{j}_b \cdot \Delta \mathbf{j}_b dA_b + \frac{1}{2} \int_{A_s} \frac{1}{d_s} \mathbf{j}_s \cdot \Delta \mathbf{j}_s dA_s \]

where,

\[ \frac{1}{2} \int_{A_b} \frac{1}{d_b} \mathbf{j}_b \cdot \Delta \mathbf{j}_b dA_b = \frac{\pi x^4}{8 d_b} \left( \hat{L} + \hat{h} + \hat{i} \right) \left( \Delta \hat{L} + \Delta \hat{h} + \Delta \hat{i} \right) \]

\[ \frac{1}{2} \int_{A_s} \frac{1}{d_s} \mathbf{j}_s \cdot \Delta \mathbf{j}_s dA_s = \frac{2\pi}{d_s} \left( a^4 g_a \Delta \hat{a} + b^4 g_b \Delta \hat{b} \right) \]

\[ g_a = \ln \left[ \frac{a}{x} \left( a + \sqrt{1 - \left( \frac{x}{a} \right)^2} \right) \right] - \frac{L}{a} \]

\[ g_b = \ln \left[ \frac{b}{x} \left( a + \sqrt{1 - \left( \frac{x}{b} \right)^2} \right) \right] - \frac{h}{b} \]

.............................(4.7)
The rate of $G_s$ in equation 4.3 is the rate of change of the internal energy minus the work done by an applied external force on the particles. Since our process is a case of pressureless sintering we obtain the following form for the rate of change of $G_s$.

$$\dot{G}_s = \gamma_s \dot{A}_s + \gamma_b \dot{A}_b$$ ........................................(4.8)

where $\gamma_b, \gamma_s =$ surface and grain boundary energies per unit area.

The perturbation of the rate $G_s$, is obtained in terms of the perturbation of the geometric parameters as shows below:

$$\Delta \dot{G}_s = \gamma_s \Delta A_s + \gamma_b \Delta A_b$$

$$\gamma_s \Delta A_s = 2 \pi \gamma_s \left( a \Delta L + L \Delta \dot{a} + b \Delta \dot{h} + h \Delta \dot{b} \right)$$ ........................................(4.9)

$$\gamma_b \Delta A_b = 2 \pi \gamma_b x \Delta \dot{x}$$

Furthermore, geometric considerations give

$$L^2 = a^2 - x^2$$ .............................................(4.10)

$$h^2 = b^2 - x^2$$ .............................................(4.10)

and volume conservation gives

$$\frac{1}{x^2} \left[ \left( a^2 L - \frac{L^3}{3} \right) + \left( b^2 h - \frac{h^3}{3} \right) \right] = \left( \frac{4}{3x^2} \right) \left( a_0^3 + b_0^3 \right)$$ .............................................(4.11)

where $a_0$ and $b_0$ are initial radii of the larger and smaller nanoparticles

Combining Eqns. 4.7-4.11 with Eq. 4.4 and using the Rayleigh-Ritz method we obtain a coupled system of linear equations of the form
where $k$ is a symmetric matrix with

\[
\begin{align*}
    k_{11} &= \frac{2\pi a^4 g_a}{d_a} + \frac{\pi a^2 L^2}{2d_b}; \\
    k_{12} &= k_{21} = \frac{\pi abLh}{2d_b}; \\
    k_{22} &= \frac{2\pi b^4 g_b}{d_s} + \frac{\pi b^2 h^2}{2d_b}
\end{align*}
\]

and

\[
\begin{align*}
    f_1 &= -2\pi \gamma_b \frac{ah(a^2 + L^2)}{x^2(h + L)} - 2\pi \gamma_s L - \frac{2\pi \gamma_s a}{x^2(h + L)} \left[ a \left( x^2 - 2hL \right) - b \left( a^2 + L^2 \right) \right] \\
    f_2 &= -2\pi \gamma_b \frac{bL(b^2 + h^2)}{x^2(h + L)} - 2\pi \gamma_s h - \frac{2\pi \gamma_s b}{x^2(h + L)} \left[ b \left( x^2 - 2hL \right) - a \left( b^2 + h^2 \right) \right]
\end{align*}
\]

Using numerical integration and solution methods for non-linear equations, the above system of equations can be solved to find the evolution of the geometric parameters $a$, $b$, $x$, $L$ and $h$ at any given nanoparticle-nanoparticle interface, in the 5-nanoparticle system under consideration. This work used Forward Euler integration with a step size of $10^{-6}$ seconds for numerical integration to update the geometric parameters and the Levenberg-Marquardt algorithm (via the inbuilt fminbnd function) in MATLAB for solution of the non-linear algebraic equations. During the first few time steps of the sintering process when the value of $x$ is near zero the numerical integration procedure is unstable. To resolve this issue we assume that the rate of change of $a$ and $b$ is zero until $x/a = 0.01$. Thus, until this condition is reached the system of equations in Eq. 4.12 reduces to

\[
x^6 = 96d_b \left[ \frac{4(2\gamma_s - \gamma_b)}{(1/a_0 + 1/b_0)^2} \right] t
\]

where, $t$ is the time since the NPs have been in contact.
Since $a=a_0$ and $a=b_0$ during this stage, the $L$ and $h$ can be found from solving Eq. 4.13 for $x$ and the using Eqn. (4.10). Note that Eq. 4.13 above is essentially a generalization of Coble’s law for free sintering. For the purposes of our model, it is assumed that densification is complete after the ratio $x/a = 0.95$. In other words, the model stops when a pill-shaped structure is formed and post necking elimination of voids and grain growth is not modeled here. The material properties used in the above sintering model are shown in Table 4.1 below.

**Table 4.1: Material properties for Ag used in the sintering model**

<table>
<thead>
<tr>
<th>Material Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_b$</td>
<td>7.12 J/m²</td>
<td>[98]</td>
</tr>
<tr>
<td>$\gamma_s$</td>
<td>1.31 J/m²</td>
<td>[98]</td>
</tr>
<tr>
<td>$\delta_b=\delta_b$</td>
<td>0.5 nm</td>
<td>[99]</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>10.27 cm³/mol</td>
<td>[100]</td>
</tr>
<tr>
<td>$D_0$</td>
<td>0.724 m²/s</td>
<td>[99]</td>
</tr>
<tr>
<td>$E_a$</td>
<td>45500 J/mol</td>
<td>[99]</td>
</tr>
</tbody>
</table>

The above described sintering model was implemented in MATLAB, and was used to track the neck geometry at each nanoparticle-nanoparticle interface, based on the temperature of the ensemble. A key input needed for this model is the temperature rise, which is obtained from the photonic heating model described in the next subsection.
4.2.2 Photonic Heating Model

The goal of this model is to predict the temperature rise in the nanoparticle ensemble as the sintering progresses. Multiple techniques such as T-matrix [101, 102], FDTD [89-91], DDA [94] and frequency domain electromagnetic FEA [95-97] can be used to predict absorption of light by nanoparticles and subsequent heat generation in the nanoparticles. Since electromagnetic FEA assumes harmonic variation of the incident electric field to reduce the time domain variable, it is computationally much faster than FDTD or DDA methods. Also, due to finite element discretization FEA can handle different shapes of the interparticle neck more easily than the T-matrix method. Therefore electromagnetic FEA in COMSOL was used in this work to model photonic heating of the nanoparticle system.

The goal of this model was to quantify the rate of heat generated by photonic heating $Q$ as a function of the ratio $x/a$, i.e., to quantify $Q(x/a)$, for the nanoparticle system. The COMSOL model (e.g. shown in Figure 4.3a) consists of five nanoparticles arranged in a plane, within a shell of air of radius $r_{air} = 350 \ nm$. Outside the air shell was a perfectly matched layer of radius $r_{PML}=700 \ nm$, used to prevent anomalous reflections of the incident electric field back into the simulation domain. Due to the natural symmetry of the system, a half model was used for computational efficiency. The above values for thickness of air shell and perfectly matched layer were chosen after multiple iterative simulations to ensure no anomalous reflections were being created by the boundary conditions. The electric field, representing the incidence of the xenon lamp light, was polarized along the $z$ direction and was travelling along the $x$ direction.
At any combination of geometric parameters the geometric modeling module in COMSOL was used for construction of desired nanoparticle ensemble geometry. The wavelength dependent dielectric constants of silver were obtained from literature, as shown in Figure 4.3b. The electrical conductivity of silver used was the same as that of bulk silver. The inbuilt electromagnetic FEA solver was used to solve for the electric field inside and outside the nanoparticles as well as the cumulative rate of heat loss (in W) in the nanoparticle system. The model was swept over wavelengths from 400 to 700 nm, over which the bulk of the xenon lamp's power is concentrated (Figure 1.5), in increments of 25 nm. Thus, for a known $x/a$ for a given nanoparticle system, curves of thermal loss vs. incident optical power as a function of optical wavelength (i.e., $Q_h/Q_I(\lambda)$) were obtained. Since the ratio of the incident optical power to the commanded light power as a function
of the wavelength (i.e., \( \frac{Q}{Q_c(\lambda)} \)) is known, the total heat generated at that particular \( \frac{x}{a} \) was obtained as

\[
Q_{\text{total}} \bigg|_{\frac{x}{a}} = \int_{\frac{700\text{nm}}{400\text{nm}}} \frac{Q_L(\lambda)}{Q_C(\lambda)} d\lambda
\]

By sampling \( Q_{\text{total}} \big|_{\frac{x}{a}} \) at different \( \frac{x}{a} \) we obtained curves of total heat generated in a given 5-nanoparticle system vs. \( \frac{x}{a} \) i.e. \( Q(\frac{x}{a}) \). These curves represent the heat flux into the 5-nanoparticle system due to photonic heating and were used as input into the nanoparticle sintering model in subsection 4.2.1. This integration is described in greater detail in subsection 4.2.3.

To obtain the function \( Q(\frac{x}{a}) \), it is necessary to obtain sample values of equilibrium geometric parameters that might occur during sintering. Note that it is important to not only obtain \( \frac{x}{a} \) but also the actual value of \( a \) and \( L \). This is because as the nanoparticles get smaller, due to diffusion from their surface into the neck, the amount of heat generated can change. To obtain sample stable geometric configurations for unmixed nanoparticles (\( a=b \) and \( L=h \) at all times and at all interfaces), the sintering model in the previous subsection was used with a constant dummy value of heat flux as input and no radiation losses. The time history of the geometric parameters was used to obtain the above sample geometric combinations of \( x, a, \) and \( L \). The procedure followed for the case of mixed nanoparticles (where \( a \) is not always equal to \( b \) at all interfaces) is described later in section 4.3.
4.2.3 Coupling Sintering and Photonic Heating of Nanoparticles

The models for photonic heating and interparticle neck growth were coupled via temperature rise and the function $Q(x/a)$, using the equations for heat transfer and the overall scheme shown in Figure 4.4. The temperature $T$ at the end of a given time step is obtained from the heat transfer equation shown in Eqn. 4.15.

$$Q = mC_p \left( \frac{\partial T}{\partial t} \right) + Q_{rad}$$

where $m$ = total mass of NPs  
$C_p$ = Specific heat capacity of NP material  
$T$ = Temperature of NP ensemble  
$Q$ = Thermal power generated by photonic heating  
$Q_{rad}$ = thermal power loss via radiation to the ambient  

The above equation does not consider transient heat conduction within the nanoparticle ensemble for the following reason. The typical time $\tau$ for transient heat conduction within a nanoparticle ensemble is dependent on the characteristic length of the system $\delta$ (equal to 5xnanoparticle diameter here) as shown in Eqn. 4.16. For example, the value of $\tau$ is approximately 26 ns for the largest nanoparticles used in this work (diameter 40 nm). This characteristic time is much larger than the minimum time step of the simulation (1 $\mu$s) and the total time of sintering (on the order of seconds). Thus, thermal conduction within the nanoparticle ensemble was neglected because the time taken for transient heat conduction to create a steady state within nanoparticles is negligible.
\[ \tau = \beta^2 \frac{\rho c_p}{3\kappa_s} \]

where
\[ \rho = \text{Mass density of NP (10490 kg/m}^3 \text{ here, for silver)} \]
\[ c_p = \text{Specific heat capacity of NP (235 J/kg.K here, for silver)} \]
\[ \kappa_s = \text{Thermal conductivity of surrounding medium (0.05 W/m.K here, for air)} \]

Thermal power losses by radiation from the surface of the nanoparticle ensemble, at any stage during sintering were calculated based on using the Stefan-Boltzmann law as shown below.

\[ Q_{rad} = A_{rad} \varepsilon \sigma (T^4 - T_{amb}^4) \]

where \( A_{rad} \) = surface area of NP ensemble over which thermal radiation occurs
\[ \sigma = \text{Stefan-Boltzmann constant} = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4 \]
\[ T = \text{Temperature of NP ensemble (in K)} \]
\[ T_{amb} = \text{Ambient temperature (298 K here)} \]
\[ \varepsilon = \text{Emissivity of silver (0.07 here, for unpolished silver)} \]

The area over which thermal radiation occurred \( A_{rad} \) was obtained from the original surface area before sintering \( A_0 \), the spherical surface area destroyed by neck growth \( A_{destroyed} \) and the new surface area created by neck growth \( A_{created} \). Eqn.4.18 shows the expressions for calculation of \( A_{rad} \) at any \( x/a \), i.e., \( A_{rad} \left|_{x/a} \right. \) for unmixed nanoparticles.

\[ A_0 = 5(4\pi a_0^2) \]
\[ A_{destroyed} = 8 \left\{ 2\pi a \left( a - L \right) \right\} \]
\[ A_{rad} = A_0 - A_{destroyed} \]

..............(4.18)
As shown in Figure 4.4, the temperature at the beginning of each time step is used to find the rate of change of $a$ and $b$ and then to update the values of $a,b,x,L,h$ by solving the non-linear eqns.4.10-4.11. Subsequently the total area of the system available for radiation and the heat generated by photonic heating (which is dependent on $x/a$) in that time step is calculated. Then, forward Euler integration is used to solve the heat transfer
equation shown in Eqn. 4.15 to update the temperature of the nanoparticle ensemble at the end of the time step.

4.2.4 Results for unmixed nanoparticles

The above modeling scheme was used to model three cases of photonic sintering of unmixed nanoparticles, with nanoparticle diameters of 10 nm, 20 nm and 40 nm. It was assumed that up to 70% of the light's power was lost during transmission, since a fiber-optic light guide was used to transmit the light to the sintering area. Further, a xenon light spot diameter of 4 mm was assumed, as measured from experiments. Figure 4.5 shows contour plots of heat generation density obtained from COMSOL simulations. It can be seen that a significant portion of the heating is concentrated at the interface between consecutive nanoparticles.

Figure 4.6 plots $Q_h/Q_I(\lambda)$ i.e., the spectrum of the thermal power generated by photonic heating per unit of incident optical power, for different values of $x/a$ and for all 3 nanoparticle sizes. For all three nanoparticle sizes a steady reduction in heat generation can be observed with an increase in $x/a$. Additionally for the 40 nm nanoparticles, there is a clear peak of heat absorption within the 400-700 nm wavelength range before any neck growth occurs ($x/a=0$). As the neck grows ($x/a>0$) this peak undergoes an observable blue shift, while reducing in magnitude.
Figure 4.5: Example contour plots of heat generation density for 10 nm particle ensembles at (a) $x/a=0$ (b) $x/a=0.06$ (c) $x/a=0.16$ (d) $x/a=0.36$ (e) $x/a=0.63$
Figure 4.6: Evolution of $Q_h/Q_i$ for ensemble of nanoparticles with diameter (a) 10 nm (b) 20 nm (c) 40 nm.
Figure 4.7 shows the total thermal power $Q_{\text{total}}$ generated by the nanoparticle ensembles, as a function of the ratio $x/a$. As expected the larger the nanoparticle the greater the amount of heat generation. In fact the heat generation for 40 nm nanoparticles is almost two orders of magnitude greater than that for 10 nm nanoparticles. However, a more critical factor to be observed is that as the neck grows ($x/a$ increases) the total heat generated can drop by almost an order of magnitude. This implies that photonic sintering is a self-damping process in the sense that the densification caused by heating reduces subsequent heat generation by the deposited nanoparticles.

Note that these results were derived using well-accepted fundamental electromagnetic FEA that is known to be capable of capturing the interaction of light with nanomaterials. For example, in this work it is able to capture the well-known effects of nanoparticle size on photonic heat generation. Therefore, it is reasonable to assume that the trends shown in Figure 4.7 are correct as well. Thus, by assuming that there is no solid-state necking and that this neck growth does not affect heat generation in the deposited nanoparticles, current photonic sintering models omit a significant trend followed by the heat source that causes sintering in the process.

Figure 4.8 shows the evolution of temperature in the nanoparticle ensembles for the three different nanoparticle sizes. The general trend of a spike in temperature followed by a subsequent stabilization or a drop can be observed. Furthermore, a larger temperature drop is observable in the case of the larger nanoparticle diameters as compared to the smaller ones, as is seen in experiments (Figure 3.15a).
Figure 4.7: Total thermal power generation by nanoparticle ensemble as a function of the ratio $x/a$.

Figure 4.8: Evolution of temperature of the nanoparticle ensemble during sintering

Figure 4.9 shows the evolution of $x/a$, $L/a$, and the radius $a$ during sintering. Figures 4.9a and 4.9b show that the 10 nm nanoparticles sinter about twice as fast as the 20 nm
nanoparticles and up to 3 times as fast as the 40 nm nanoparticles. This correlates well with experimental observations which show that under the same power and for the same sintering time smaller nanoparticles undergo much greater densification than larger nanoparticles.

Figure 4.9c shows that the nanoparticle radius also reduces during densification, probably due to surface diffusion being a dominant effect in nanoparticle sintering. Since the driving force behind neck growth is the need to reduce surface energy, the faster rate of sintering for smaller nanoparticles is because of the larger surface area to volume ratio of the smaller nanoparticles. In other words, photonic sintering is affected by a competition between the amount of energy that is needed to drive neck growth to completion vs. the reduction in photonic heating with densification. Both of the above factors depend significantly on the nanoparticle size, explaining why nanoparticle diameter has such a significant influence on densification in the process.
Figure 4.9: Evolution of (a) Ratio $x/a$, (b) ratio $L/a (=h/a)$ and (c) nanoparticle radius $a$, obtained from developed photonic sintering model.
To examine the difference between the developed model and current models in literature, in terms of the ability to capture the physics of photonic sintering, we obtained predictions from our model with a constant heat generation by the nanoparticle ensemble irrespective of the neck size. For each nanoparticle diameter this constant value was the initial total thermal power generated at $x/a=0$. This effectively assumes that the amount of photonic heating $Q_{\text{total}}$ throughout the sintering process is equal to that obtained by experimentally characterizing the absorption spectrum of the as-deposited nanoparticles.

Figure 4.10: Evolution of temperature of the nanoparticle ensemble when heat generation is assumed to be independent of sintered geometry of nanoparticle ensemble

Figure 4.10 shows the predicted evolution of nanoparticle ensemble temperature under the constant $Q_{\text{total}}$ assumption. Note, that the predicted temperatures are much higher
than in the case where $Q_{total}$ is dependent on $x/a$ (Figure 4.8). The characteristic spike and subsequent dip in temperatures, seen in both experiments and with the assumption of $x/a$ dependent $Q_{total}$ in the developed model, have disappeared. The reason for this change in trend can be explained by comparing the heat generation by photonic sintering ($Q_{total}$) to the heat loss by radiation ($Q_{rad}$) for the cases where $Q_{total}$ is constant (Figure 4.11) and where $Q_{total}$ is dependent on $x/a$ (Figure 4.12). For the constant $Q_{total}$ assumption, (Figure 4.11) the $Q_{rad}$ catches up with the $Q_{total}$ at a much later stage of neck growth than it does for the case of the $x/a$ dependent $Q_{total}$. Furthermore, in the constant $Q$ case the $Q_{rad}$ does not exceed $Q$, thereby resulting in a flatter temperature profile.

![Figure 4.11: Comparison of $Q$ (photonic heat generated in solid red) and $Q_{rad}$ (heat loss via radiation in dotted blue) under the constant $Q$ assumption](image)

10 nm dia. nanoparticles  
20 nm dia. nanoparticles  
40 nm dia. nanoparticles
When the $Q_{\text{total}}$ is dependent on $x/a$ (Figure 4.12), the reduction of $Q_{\text{total}}$ with increasing $x/a$ enables heat losses $Q_{\text{rad}}$ to catch up with $Q_{\text{total}}$ much earlier on during the sintering process. This causes a reduction in temperature after the initial temperature spike and is the reason for the trends seen in Figure 4.8.

Note that (1) a change in photonic heat generation with a change in ensemble geometry is a fundamental physical effect that arises from basic behavior of light interacting with nanomaterial ensembles; and (2) neglecting this effect is not able to capture the trends for temperature evolution seen in photonic sintering. Therefore, current models of photonic sintering which assume constant $Q_{\text{total}}$, by neglecting any effects of necking on heat generation, omit a key physical phenomena in the photonic sintering process.
The evolution of the geometric parameters (Figure 4.13) under the constant $Q_{total}$ assumption shows that faster sintering of smaller nanoparticles is still captured. At the same time, a comparison to Figure 4.9 shows that the predicted sintering time is orders of magnitude lower under the constant $Q_{total}$ assumption. This is because the predicted temperature rise is much higher and faster, as shown in Figure 4.10. Since this trend of faster temperature rise is because the physical dependence of $Q_{total}$ on $x/a$ is not accounted for, current models of photonic sintering overestimate both temperature rise and densification during photonic sintering.

For example, the temperature trends in Figure 4.10 and the depression of melting point for Ag nanoparticles (Figure 4.14, from [103]) show that current models would predict melting of the 40 nm diameter nanoparticles. However, as is seen in chapter 3 the sintered structure for 40 nm nanoparticles shows neck growth but little melting. Note that lower melting temperature of silver nanoparticles is due to the relatively large ratio of surface atoms to inner atoms [103, 104]. The high proportion of surface atoms drastically decreases the melting temperature, because the surface energy of the unbound surface atoms is extremely high. The overestimation of temperature and densification by current photonic sintering models has a significant practical impact on the ability to control density of the sintered material and temperature rise of the substrate.
Figure 4.13: Evolution of (a) Ratio \( x/a \) (b) ratio \( L/a \) and (c) nanoparticle radius \( a \), obtained from developed photonic sintering model under the constant \( Q \) assumption.

Figure 4.14: Melting point of Ag Nanoparticles as a function of nanoparticle diameter
4.3 Mixed Nanoparticles

This subsection describes the modifications made to the model described in section 4.2 to model photonic sintering of mixed nanoparticles.

4.3.1 Modeling method

The evolution of the interface geometry between differently sized nanoparticles is different from that between nanoparticles of the same size. For example, a smaller nanoparticle between two larger nanoparticles will be absorbed into the bigger nanoparticles [88] during sintering. To account for these effects, the following modifications were implemented in the sintering model from Section 4.2.

1. In the sintering model, the criterion for terminating the simulation was changed to \( \frac{x}{b} > 0.95 \). This signifies that the simulation is terminated when the smaller nanoparticle has been completely absorbed into the larger nanoparticle at any given interface. Note that when the two nanoparticles at any interface are of equal size, i.e., \( a = b \), then the condition reduces to \( \frac{x}{a} > 0.95 \) as in the previous section.

2. The above modified sintering model was also used to obtain the sample values of equilibrium geometric parameters from which the function \( Q(x/b) \) were derived via COMSOL simulations. Again \( Q \) was defined as a function of \( x/b \) because it was known that the ratio \( x/b \) will grow faster than \( x/a \). In this case the geometric parameters were \( a, b, x, L \) and \( h \) at each interface. Note that in the case of equal sized nanoparticles \( a=b \) and \( L=h \), so that it is sufficient to use only \( a, x, \) and \( L \) at interfaces where the nanoparticles are of equal size.
(3) The area over which thermal radiation occurred $A_{x/a}$ was obtained as in subsection 4.2.3. However, in this case the $A_{\text{created}}$ and $A_{\text{destroyed}}$ were calculated at each neck as shown in Eqn. 4.19, before being summed.

$$A_0 = 4\pi \left[ n_{\text{larger}} \left( a_0^2 \right) + n_{\text{smaller}} \left( b_0^2 \right) \right]$$

$$A_{\text{destroyed}} = \prod_{\text{interface 1 to 4}} 2\pi \left[ a(a-L) + b(b-h) \right]$$

$$A_{\text{rad}} = A_0 - A_{\text{destroyed}}$$

where,

\begin{align*}
n_{\text{larger}} &= \text{number of larger NPs}; \quad n_{\text{smaller}} = \text{number of smaller NPs}
\end{align*}

Two different nanoparticle ensemble configurations (shown in Figure 4.15) were used to capture the effects of diametrically opposite weight ratio of smaller to larger nanoparticles, on densification and temperature rise during photonic sintering. The nanoparticle diameters considered were 10 nm and 20 nm. The interfaces shown in Figure 4.15 are for ease of explanation in the next subsection. Note, in the below configurations the percentage by weight of the larger nanoparticles is greater in configuration A than in configuration B.
4.3.2 Results

Figures 4.16 and 4.17 compare the evolution of the ratios $x/a$ and $x/b$ at each interface for both configurations shown in Figure 4.15. In configuration A (Figure 4.16), the ratio $x/a$ equals $x/b$ at interface 1 since two similarly sized nanoparticles are in contact at this interface. Further this value of $x/a$ goes up to around 0.45. The values of $x/a$ and $x/b$ at interface 2 are different because two nanoparticles of different sizes are in contact with each other – $x/a$ is lower than $x/b$ at interface 2 simply because $a>b$ at any point of time during sintering. The fact that $x/b$ at interface 2 reaches a value greater than 0.95 first shows that the smaller nanoparticle at this interface is being absorbed into the larger nanoparticle.
Figure 4.16: Evolution of geometric parameters at each interface for configuration A

(a)

(b)
Figure 4.17: Evolution of geometric parameters at each interface for configuration B
In configuration B (Figure 4.17), \( x/a = x/b \) at interface 2 since two the two nanoparticles in contact have the same size. This value of \( x/a \) at interface 2 goes up to about 0.75 and \( x/a \) is lower than \( x/b \) at interface 1, since two nanoparticles of different diameter are in contact. The fact that \( x/b \) at interface 1 reaches a value greater than 0.95 first indicates that the smaller nanoparticle at this interface is being absorbed into the larger nanoparticle.

A key difference that can be observed between the two configurations is that the maximum \( x/a \) for interface 1 for config. A = 0.45 and the maximum \( x/a \) for interface 2 for config. B = 0.75. Therefore, the degree of densification of nanoparticles at interface 2 in configuration B is greater than that of nanoparticles with interface 1 in configuration A. In other words, by the time the smaller nanoparticles that are sandwiched between the larger nanoparticles have been absorbed into the larger ones, the degree of densification achieved by the smaller nanoparticles in configuration B is greater than that achieved by the larger nanoparticles in configuration A.

Thus, in configuration B a number of smaller nanoparticles are being sintered to a greater density while enclosing a larger nanoparticle that is not densifying as quickly. This is the converse of what happens in configuration A. Thus, densification is higher, under the same incident optical power and sintering time, when the ratio of smaller to larger nanoparticles by weight is increased. This effect is seen experimentally as well in Figures 3.10-3.14 in Chapter 3.
Another important factor to note is that the temperature rise in the mixed nanoparticle ensemble (Figure 4.18) is higher than that for an ensemble of pure 10 nm nanoparticles but lower than that for pure 20 nm nanoparticles. This is because, while larger nanoparticles in the mixture are responsible for producing more heat than would be possible with unmixed smaller nanoparticle inks the presence of smaller nanoparticles reduces the mass of the ensemble and increases the net surface area per unit volume. This is another reason why densification of mixed nanoparticles is much faster in configuration B than in an unmixed 20 nm nanoparticle-ink. Basically the larger nanoparticles act as local sources of high heat while the rest of the smaller nanoparticles use this heat to sinter around them.

While the above comparison of temperatures between mixed and unmixed nanoparticle-inks as well as the general trend of a temperature spike followed by a steady state temperature is reflected in experimental results from chapter 3, it should be noted that the developed model also predicts a 50°C difference between peak temperatures for configurations A and B. This is not reflected in experimental findings in Figures 3.10-3.14, indicating that further research is needed to tune the model for mixed nanoparticle-inks.
Figure 4.18: Predicted temperature evolution during sintering for configurations A and B

4.4 Summary and Inferences

To summarize, the modeling effort described in this chapter uses an implicit coupling between photonic heating of nanoparticles and neck growth between nanoparticles to uncover fundamental nanoscale phenomena in the process. It is shown that the developed model reflects experimental trends seen in Chapter 3. Further, the completeness of state-of-the-art modeling assumptions are examined as well. Key inferences regarding the physics of photonic sintering that can be drawn from the presented results are:

(1) Photonic sintering is a self-damping process because neck growth caused by heating reduces subsequent heat generation by the nanoparticles, i.e., the desired effect of interparticle neck growth also acts to inhibit further neck growth during
the process. Thus current models in literature omit a significant physical effect in photonic sintering when they make the assumption that there is no neck growth and that it does not affect photonic heating of the nanoparticles. As a result current models significantly overestimate the temperature rise and the density of the sintered material, resulting in an inability to control the sintered material density and temperature. An example of a practical issue that can arise as a result of this loss of control is the use of greater than necessary lamp power and sintering temperature, resulting in higher rise in substrate temperature and consequent damage to the substrate. Additionally, this self-damping behavior is also the probable reason behind the observation in literature that there is no observable increase in densification after a certain number of flashes in flash-lamp based photonic sintering despite significant porosity still observable in the sintered material.

(2) Densification in photonic sintering is affected by a competition between the energy needed to drive sintering kinetics to completion and the concurrent reduction in photonic heating with densification. Both of the above factors depend significantly on the nanoparticle size, which is why nanoparticle diameter has such a significant influence on densification in the process.

(3) Mixing of nanoparticles of different sizes generates temperatures that are intermediate between pure inks of the two different nanoparticle sizes. At the same time, increasing the ratio by weight of the smaller nanoparticles to the
bigger nanoparticles increases densification. This is because the larger nanoparticles act as local sources of high photonic heat generation. This heat is transferred via conduction to the smaller nanoparticles, resulting in rapid neck growth between the smaller nanoparticles, even though the neck growth between the smaller and larger nanoparticles is slower. Thus, the larger nanoparticles get embedded in a matrix of sintered smaller nanoparticles. This indicates that design of nanoparticle sizes and nanoparticle size distributions in a nanoparticle-ink is a key element needed for control of the photonic sintering process.

Consideration of the new nanoscale phenomena uncovered here is critical to realizing the full potential of the photonic sintering process.
Chapter 5: Design and Feasibility of Xenon-Light-Additive-Manufacturing-Process (LAMP)

This chapter describes the design and testing of a prototype system developed in this work to integrate photonic sintering with inkjet deposition towards a low-cost, desktop and multi-material capable additive manufacturing system. The overall system will be described in section 5.1, followed by detailed descriptions of the design and functionality of each subsystem in sections 5.2-5.5, as well as the details of integration of those subsystems in section 5.6. Next, ink development and jetting parameter optimization will be covered in sections 5.7-5.8. The results of a series of dynamic deposition and sintering tests will be presented in Section 5.9 and lastly, a chapter summary will be presented in sections 5.10.

5.1 LAMP prototype overview

The developed LAMP prototype system consists of the broad spectrum xenon-light source (from earlier chapters) and a piezoelectric inkjet head combined onto a single system (Figure 15.1) consisting of a three-axis motion stage, a well plate to store nanoparticle inks and a variable temperature hot plate on which the substrate is placed.
The cost of this functional prototype was approximately $20,000, which is much lower than traditional metal additive manufacturing processes such as selective laser sintering and direct metal deposition. The system is multi-material capable due to the broad spectrum nature of the light source, e.g., metal (Silver), doped semiconductor (AZO), conducting oxide (ITO) and ceramic (WC) nanoparticles were sintered using this system.

The following sections describe the design and integration of the subsystems of this prototype system. The key aspects of the design and construction of the overall system are described in the following order:

5.2: Inkjet Head: For depositing nanoparticle inks

5.3: Motion Stage: For motion of the co-mounted inkjet head and light source.
5.4: Xenon Light Source: For delivering xenon light to the deposited nanoparticles.

5.5: Hot Plate: For holding the substrate at slightly elevated temperature when needed.

5.6: Integration of Subsystems: Software and hardware integration of subsystems.

5.7: Jetting Parameters and Ink Development: Preliminary testing of the inkjet with different solvents for the nanoparticle inks.

5.8: Deposition Optimization Tests: Optimization of inkjet deposition speeds and feeds and toolpath.

5.9: Dynamic Sintering Tests: Automated deposition and photonic sintering of nanoparticles.

This above order is chosen so as to most effectively describe the designed and fabricated system to the reader. The first four sections (5.2-5.5) describe the individual subsystems within the system. The last four sections (5.6-5.9) deal with subsystem integration and preliminary testing of the system.

5.2 Inkjet

The inkjet head is a piezoelectric-driven single-orifice dispense head manufactured by Engineering Arts. The piezoelectric device at the core of the dispense head is driven by proprietary DE03 circuitry. The dispense head is activated by energizing the piezoelectric material with a sine, square or trapezoidal wave. In practice, the amplitude of the wave determines how energetically the droplets are expelled from the orifice, and is set by an
11 bit variable (11 bit variables provide a range from 0-2047). Droplets are generated at a frequency typically ranging from 11500 to 13500 Hz and can be controlled down to each individual drop that is dispensed through either a 32 or 67 micron orifice. The system schematic is shown below, in Figure 5.2.

Figure 5.2: Inkjet fluidics schematic

In the above diagram, the fluid path is illustrated, with flow starting at a filter (component 1) within the fluid reservoir (component 2) which keeps any impurities large enough to potentially cause a nozzle clog out of the fluid path. The degasser (component 3) is used to remove dissolved gas and small bubbles from the water being supplied to the jet. Although the system can operate without this component, it is more reliable with the degasser installed since small bubbles trapped in the nozzle can prevent operation of the inkjet by absorbing much of the energy pulse (air is compressible and the displacement produced by the piezoelectric element is very small). The syringe pump (component 4) is
used to draw liquid in and out of the inkjet head, as well as for flushing the nozzle. During inkjet operation, however, the syringe pump is bypassed, creating an open path from the fluid reservoir to the inkjet tip. Components 5 and 6 are fittings that join sections of tubing and adapt between tubing of different diameters. The inkjet dispense head (component 7) terminates the fluid path.

The most sensitive portion of the entire system is the lines of fluid path. These fluid path lines are sensitive to vibration and impact, either of which can cause jetting failure by causing air to be pulled into the nozzle. Although the schematic shows the inkjet above the level of the reservoir for nanoparticle inkjetting, reliability is increased by positioning the level of the reservoir slightly above the inkjet orifice. Since it takes a higher amplitude of the driving wave to initiate droplet generation when using nanoparticle inks, this positive pressure aids in starting the flow. The reservoir height can be adjusted as the fluid is depleted or to tailor the pressure to each individual ink by using a lab jack as shown in the Figure 5.3 below. For troubleshooting of the inkjet, refer to Appendix A.
Another important component in the inkjet system is the side camera. The camera used in this application is a USB CMOS (p/n UI-1220SE-M) with a 5X lense and a working distance of 20mm. The inkjet nozzle can be moved in front of the inspection camera to check the condition of the nozzle or check how consistently it is generating droplets. Images of jetting with both the 32um and 67um nozzle orifices can be seen in the figure below.
5.3 Motion stage

The initial search for motion stage solutions began with identification of the most
ingredient design parameters. These factors are given below in order of relative
importance:

1.) The stage needed to be easily integrated with other components of the system.
   It needed mounting points to attach custom brackets to hold the inkjet and the
   light guide. Further, it should integrate with the software that controls the inkjet.
   Ideally, the system should be programmable such that coordination between
   motion and deposition timings is possible.

2.) The stage needed to be relatively inexpensive, since one of the main motivations
   was to design a low-cost system. As such, the motion stage should be constructed
using as many off-the-shelf as possible. In case of a failure, the system needs to be easy to repair to limit downtime.

3.) The motion stage needs to be accurate within approximately 10 µm in all directions to repeatedly position the inkjet for multiple layer deposition.

4.) The motion stage solution should be able to interface with components that are not necessarily off-the-shelf. Having extra digital and analog input/output pins on the control board for communication with external devices would be an advantage.

The motion stage that was chosen is driven by Schneider Electric stepper motors with position feedback and Misumi ballscrew linear guides on all three axes. The motors communicate using full duplex RS-485, i.e., all three motors can be wired in series using a single RS-485 cable. Each motor has an integrated controller that can be independently programmed to interpret the commands sent over the common line and move accordingly.

A prototype board developed by Engineering Arts was used for motor power and data distribution. Other electrical components including cabling and a Cosel PLA600F-48 600W 48v switching power supply were purchased from Mouser and the Oregon State University IEEE store. The z-axis linear guide has four M3 tapped holes which are used as mounting locations for the inkjet and light guide. The parts needed to interface the linear guides and other components were custom made, and will be discussed in more detail.
later in this chapter. The motion stage assembly drawings are shown below in Figure 5.5.

A picture of the assembled motion stage is shown in Figure 5.6, below.
After assembly, each motor had to be individually wired and programmed. With all three motors set to full duplex party mode, the RS-485 connections were wired in series for simultaneous control via the software, i.e., serial commands are sent preceded by a unique identifier for the motor the command is intended for. Each controller actively listens on the shared line, and parses the commands, responding only to the ones preceded by its identifier. Details on programming and wiring can be found in Appendix C.

Based on vendor specifications, this motion stage is much more accurate than the design requirements, with 2.5 micron accuracy in the X-axis, 1.25 microns on the Y-axis and 0.625 micron accuracy in the Z-axis. The range of travel is 400mm in X, 250mm in Y and 100mm
in Z. Each motor is running at a software limited 75% of full design current to provide adequate torque for individual axis feedrates of up to 400mm/s without stalling of the stepper motors. While there are no input/output pins on the motion stage, the RS-485 communication can be used to communicate with an independent microcontroller if more input/output capability becomes necessary.

Since the Engineering Arts software for control of the inkjet was developed for use with Schneider Electric motors – motion control of the stage is fully integrated into the program. With the code developed during this project (coding examples can be found in Appendix B), the Engineering Arts software can create the necessary motion for building basic two dimensional and three dimensional shapes.

5.4 Light source and guides

5.4.1 Light Source

Initial thoughts around choice of xenon light source were to use a pulsed light sources similar to that used in literature. The motivation for using a pulsed light source by previous investigators was to avoid damage to the substrate on which the nanoparticles are deposited. Since the light source would be in continuous motion for our system it was determined that a continuous xenon light source, with a flexible fiber optic light guide to deliver light to the deposited particles. In this way, the ability to sinter nanoparticles without damage to the underlying substrate is retained, and the relative complexity of the system as compared to a pulsed light source with a larger spatial footprint is decreased. Aside from the reduction in complexity other advantages of using a
continuous light source include reduced power consumption, the ability to control which spatial region of deposited nanomaterial receives optical energy, and the ability to control the rate at which optical energy is delivered by easily varying the motion speed of the lighter light source. To determine how much power was needed, a spreadsheet was constructed to calculate the power deposited to the particles based on estimated losses, light spot diameter, motion stage feedrate and existing threshold energy values for photonic sintering in literature. With a very conservative estimate of 28% transmission of optical energy to the substrate, the target value of 60 J/cm² necessary to sinter metallic particles from previous research (see chapter 2), could be reached at feedrates of up to 50mm/s. With these factors in mind, a PerkinElmer XL3000 equipped with a 300 watt Cermax high pressure xenon bulb was chosen as the light source.

Figure 5.7: PerkinElmer XL3000

This source emits a broad spectrum of light covering the entire visible range as well as extending slightly into both the infrared and ultraviolet wavelengths which is then
focused and collimated into the fiber optic light guide – allowing it to be easily delivered to the desired location. The spectral output data (as given by the manufacturer) is shown in Figure 5.8, below.

Figure 5.8: 300W Cermax Xenon Spectral Output

The XL3000 has several advantages over other light sources on the market. First, it is relatively inexpensive at $3500 and has a long bulb life (1000 hours manufacturer claimed lifespan) – when running the machine on average 2 hours per day, the bulb should last for nearly two years. In a commercial setting, the bulb replacement interval would be significantly shorter due to the fact that the machine would be on with the bulb burning for a large percentage of each day. When bulb replacement is required, the bulbs are inexpensive and easy to change.

Another advantage of this light source is the built-in aperture that can be controlled via RS-232 serial communication. This allows the user to set the intensity of the light entering
the cable to 255 unique levels quickly via software. Using the free program Terminal (Which can be found at https://sites.google.com/site/terminalbpp/), scripts can be written to command the light source execute sequences of events. Example code can be found in Appendix C. Other systems available at this price point have similar aperture control, but it must be adjusted by manual user input.

Using a light source with broad spectral output is important because the absorbtance of light by nanoparticles depends on many factors, including material type, size and shape of the particle. For example, gold nanoparticles have peak absorption of light between 515-572nm depending on nanoparticle size, while silver nanoparticles absorb light at wavelengths between 410-500nm most efficiently. This phenomenon is shown in Figure 5.9. Therefore broad spectrum light can be absorbed by a wide range of nanoparticle materials, sizes and shapes. This provides a multi-material capability to the additive manufacturing system.
5.4.1 Light Guides

Since it is advantageous to transmit as much light as possible from the xenon bulb to the substrate, Fiberoptix Inc. were contracted to manufacture a fiber optic light guide to our specifications. Two different light guides, one with a 3.5mm bundle diameter (the largest possible for our source), and one with a 1.5mm bundle diameter were obtained. Both were two feet in length, with M8x1.25 threads on the distal end for mounting to the motion stage. The 3.5mm bundle diameter yielded better transmission efficiency – the spot size was larger and the intensity appeared nearly equal if not slightly brighter than the 1.5mm bundle guide. This is mostly due to the 3.5mm bundle having the ability to
capture a much higher fraction of the light supplied by the source. The majority of the light never gets into the bundle on the smaller guide (see Figure 5.10, below).

![Figure 5.10: 1.5mm (left) and 3.5mm (right) bundle diameter light guides](image)

The outside diameter of the light guide is 5.35mm, so the bundles of the 1.5mm and 3.5mm guides are up 42.8% and 18.4% respectively of the total area of the light guide end. Since the intensity of the light incident on the light guide end at the source most likely decays towards the outer edge, the guides may pick up a higher percentage of the total light energy. In any case, the smaller bundle diameter guide is at a severe disadvantage to the larger guide in terms of transmission efficiency. If the 1.5mm guide was made with a tapering bundle that started out at a larger diameter and tapered to a smaller diameter at the distal end, the transmission efficiency would be greatly increased.

### 5.5 Hot plate

The last component needed to complete the system was a heated surface on which to place the sample substrates, if needed. It needed to be a very low lying platform to fit within the limited Z-travel of the system, as well as fit within the limited space of the X-Y plane – a space shared with other system components. The plate needed to be able to automatically regulate temperature from ambient up to about 120°C. We searched for an
off the shelf hot plate that fit the requirements, but no suitable model was found, so a custom plate was designed and fabricated.

In order to fulfill the requirements above, a slim heated board was selected (originally designed for a PrintrBot Simple). The board takes a 12v electrical input and has the dimensions of 4.65 x 7.25 inches. The dimensions of the heated board were well suited to the space available on the motion stage, and the mounting points were very close to the threaded holes on the base plate of the stage, so it was easily adapted to the spacing with custom mounts combined with standoffs to raise the plate up slightly. The hot plate was covered with a glass plate to protect it from the conductive nanoparticle bearing suspensions as well as to act as a thermal reservoir.
To provide temperature feedback, an Arduino Uno Rev3 microcontroller was utilized in conjunction with a 100kΩ thermistor with a 4066 β-coefficient. Power to the board was controlled by a relay module that can be switched by a digital pin on the Arduino board to provide a ground to the coil of the relay through a transistor by pulling the gate pin to 0v to allow current to flow across the transistor. The software then monitors the temperature of the hot plate, comparing it to the target temperature and switching power on or off accordingly. The hot plate status is outputted to a small 16x2 LCD screen, indicating on line two first the current temperature followed by the target temperature followed by the heater status in the following format: T(current temperature)/(target temperature) (Heat status). The display is seen below, in Figure 5.12.

![Hot plate display](image.png)

*Figure 5.12: Hot plate display*

With the integrated display, the hot plate can be operated independently of a computer, but the temperature must be set in the code using the Arduino compiler. If the need arose, a potentiometer or buttons could be added to the system to allow adjustment of
temperature independent of the compiler. In later iterations of LAMP, all the subsystems would be integrated and able to communicate with the main controller.

5.6 Integration of subsystems

5.6.1 Hardware Integration:

Before the first full system tests could be run, all the subsystems needed to be integrated with the motion stage. To accomplish this, parts were designed to adapt the mounting of each component to the others, using a modular design to facilitate easy modification to the system. The integration assembly consists of three parts, which are shown in grey in the CAD rendering. Each component is designed to interface with only one subsystem, which permits rapid modification of the system if the need arises.

The light guide mount interfaces the fiber optic light guide with the carrier. Several versions of this component have been designed and manufactured, allowing the light guide to be mounted in different positions or orientations by swapping only the light guide mount. The vertical light guide mount is shown in the rendering, while the 45° mount is shown in the photograph in Figure 5.13. The carrier interfaces with both the light guide mount and standoff, but only directly interfaces with the inkjet subsystem. It carries the inkjet, which can be manually adjusted in the Z-direction, as well as providing mounting locations for the electrical and fluidic connections needed to support inkjet operation. Lastly, the standoff interfaced the carrier and light guide mount to the motion system. Any changes in position or orientation of the assembly can be accomplished by replacing the standoff. The 90 degree standoff is shown in the figures.
The hot plate is integrated in a similarly modular manner – rather than drilling holes for the plate, a bracket was designed that adapts the plate mounting holes to the uniform
hole spacing present on the motion system base plate. By using an adapter, the mounting location is more flexible – the position of the hot plate position and the well plate could be swapped in less than five minutes.

5.6.2 Software Integration:

The current revision of the software fully integrates the motion stage with the inkjet system. Without integration of these systems, the prototype would not be functional. Integration of the hot plate and light source is not complete, but future software updates will allow for full control of the light source through the built in RS-232 commands, as well as being able to control the hot plate temperature setting. In this way, the light levels could be precisely tuned to match the substrate temperature, gantry feedrate and the operating conditions of the inkjet. As an example, the aperture of the light source could be completely closed when the system is drawing an ink sample in order to prevent light exposure to the ink(s) in the well plate.

5.7 Initial jetting parameters and ink development

Before the Engineering Arts dispense system was purchased, it was evaluated at their labs on the Arizona State University campus. During this evaluation, the jet was tested with two nanoparticle suspensions. At the beginning of every use as well as before the system is shut down, distilled water is jetted to set a baseline on nozzle operation as well as check nozzle functionality. The nozzle operated as expected when using water, dispensing very consistent spherical droplets with uniform spacing.
When running an ink, the system is programmed to draw up a user defined quantity from a programmed location, in this case a specified well in a 96 well plate. Once the ink is drawn, the system can be commanded to dispense the ink. Once the ink that has been drawn into the nozzle is exhausted, the motion system can be programmed to automatically return the nozzle to the ink well to draw another column of liquid. If programmed properly, and using a well-tuned ink, the integrated system can theoretically run until the ink reservoir in the well plate is depleted.

While these tests gave enough of an indication that the system would be serviceable with nanoparticle inks, it also made clear that ink tuning would be required to yield reliable jetting performance. Rather than formulate a wide variety of inks, a more sequential approach was adopted: first a variety of pure solvents were tested, followed by ink development using the solvent(s) that flowed most readily. The system was designed for water use and was very reliable using water so this was the most obvious choice for a solvent, but from previous ink development from before the system was assembled it was known that suspensions of nanoparticles using other solvents yielded an ink that was much less prone to separation. With this previous knowledge, the system was tested by drawing samples of water, ethanol, and tetradecane.

Water ran flawlessly, as expected. Ethanol also jetted well, but required slightly higher excitation energy to be applied to the piezoelectric drivers to get a droplet stream started. It also had the problem of quickly diffusing into the water column in the lines supplying the inkjet – after a short period of time, the sample was so diluted that it jetted identically
to water. In order to solve this problem, the system could either be completely flushed and filled with ethanol or a small sample of colored silicone oil be drawn before drawing a sample of ethanol. Another problem with running pure ethanol was evaporation off of the tip, which was expected to cause some reliability issues with suspended particles from the experience with butyl acetate. Since pure ethanol offered little advantage over water for suspension of nanoparticles, we chose not to pursue it as a solvent any further.

Lastly, tetradecane was tested in the inkjet. Tetradecane had been used successfully in previous tests suspending the nanopowders and there was also an ink commercially available that exhibited very promising results when deposited and sintered in static tests. With this in mind, we were willing to go to greater lengths to get the inkjet running with tetradecane. Unlike the two previous solvents, tetradecane did not diffuse into the water, but proved to be quite hydrophobic. This, combined with it wetting glass well, produced new problems. First, it would not jet reliably, even with high amplitude excitation commands to the inkjet. When it did flow, it was inconsistent and often required intermittent manual wiping of the inkjet nozzle with a swab to initiate flow. A secondary problem emerged when a second sample was drawn, small droplets of both tetradecane and water clung to the inside of the nozzle adding to the jetting problems. This problem could be corrected by backflushing the nozzle with methanol to dissolve flush away both the water and tetradecane, so no permanent damage was done to the inkjet.

After the above testing, the decision was made to continue ink development using water as a solvent, and to ultrasonicate the ink prior to running it to (temporarily) resolve as
much of the separation issues as possible. After a series of tests to determine optimal
nanoparticle concentration for inkjetting, 1% particles by weight was chosen – that was
the highest concentration that would reliably flow though the inkjet. Variations of 1%
inks were used for the remainder of the testing that was performed using the inkjet.

5.8 Deposition optimization tests

5.8.1 Single lines

After the basic jetting parameters were established with the 1 wt% 20nm Ag ink, a series
of tests were run to determine the optimal path for depositing multiple layers of material
into a continuous structure. Since developing optimal deposition parameters was the
goal of this subsection, the light source remained off.

1.) A series of 10 layer lines were deposited on substrate temperatures varying from
30-120°C at a feedrate of 240mm/s. At 120°C the deposited lines showed the least
spreading, so this value was chosen for further tests. Next, the same 10 layer lines
deposited onto three different substrates (glass, brass and aluminum) with all
other parameters held constant from the previous test. Figure 5.15 shows the
results of these tests.

Figure 5.15: Single 10 layer lines on glass (left), brass (center) and rolled aluminum
(right)
Since the most consistent lines were generated using a rolled aluminum substrate all subsequent tests were run on aluminum.

2.) The next series of tests varied the feedrate of the gantry from 240 to 300mm/s, while holding all other parameters constant. A feedrate of 285mm/s was found to create the most consistent 10 layer lines on rolled aluminum. Both an optical microscope image as well as an interferometer scan of the surface of a single line created using a feedrate of 285mm/s are shown in Figure 5.16.
Since the rough surface finish of the rolled aluminum made geometric characterization of the deposited structures difficult, test series (2) was re-run using mirror finish aluminum, arriving at an optimal feedrate of 300mm/s.
3.) The next series of test held all parameters constant in order to generate a set of samples from which an average line width could be determined. Five additional individual 50 layer line samples (for a total of six) were deposited using a feedrate of 300mm/s, onto mirror finish aluminum held at 120°C. The line structure from this test is shown in Figure 5.17. Unlike the line made on rolled aluminum, the profile of the line could be easily recognized on the mirror finish aluminum. The total width of the deposited lines were measured using an optical microscope, yielding an average width of 243 microns. This width was used to calculate the toolpath for 20% to 70% in-the-plane overlap between consecutive lines in the next subsection. All subsequent tests were run on mirror finish aluminum to allow accurate measurements of thickness and profile.
5.8.2 Multiple lines

The next step was to determine the parameters for enlarging the width of the structures in the plane of the substrate by overlapping multiple lines in the Y-direction. There were
three key differences between the multiple line deposition in this subsection and single line deposition in the previous subsection, namely:

(1) Multiple lines were deposited in the plane of the substrate to widen the width of the line made on the substrate. The in-plane (XY) overlap between the consecutive lines was varied to find the optimal overlap needed to create a dense line after sintering. The toolpath pattern followed, i.e., whether multiple Z-layers should be deposited first a single line or multiple in-plane lines should be deposited creating a single Z-layer, building the structure layer by layer was examined.

(2) Different number of layers were deposited in the Z-direction to examine the change in structure height and width due to the addition of more material.

(3) In all experiments, deposited nanomaterial was exposed to light at 100% light source power at a feedrate of 1mm/s (corresponding to 4 seconds of sintering time at one spot) after deposition was complete.

The following depositions were created using a toolpath that made a single layer by depositing five lines in the XY plane, and then returning to the original XY location to start the next layer. This path was repeated 50 times to create a structure that was 5 overlapped lines wide (top to bottom) and 50 layers thick, for a total of 250 depositions. Figure 5.18, below, shows effect of overlap between consecutive in-plane lines, starting with 20% overlap and ending with 70% overlap. Two observations can be made here. First, a higher overlap of around 70% is able to create structures with minimal gaps between the lines. Secondly, at a 70% overlap the total width of the structure is expanded to
around 500 microns (Figure 5.19) from around 243 microns for single line deposition (Figure 5.17).

Figure 5.18: Overlap study
Next the effect of the toolpath itself was examined. As compared to the above toolpath, the next toolpath deposited 50 lines in the same location before the inkjet moved on to the adjacent XY position to deposit the 50 layers for that line. The sintered line with an XY overlap of 70% can be seen in Figure 5.20. Using this toolpath, the width of the total line is lower and that the surface is not as smooth as in the case of the previous toolpath.
Figure 5.20: Sequential line deposition

The effect of the number of Z layers deposited per line before sintering on the total line width was also examined. Tests were run at 70% overlap with layer thicknesses ranging from 20 to 100 depositions. The measured line widths (Figure 5.21a) show that the lines
remained approximately 550µm wide up to a thickness of 50 depositions. After this point, the lines began to widen to 659µm at a thickness of 100 layers. A layer thickness of 50 depositions per line, before sintering, seems to be optimal to prevent the structure from spreading significantly outside the toolpath.

Further, the effect of the number of Z layers before sintering, on the total thickness and quality of the sintered line was also examined using a ZeScope white light interferometer to measure the profile of the deposition on the same set of samples. Figure 5.21b, shows that thickness of the sintered structure consistently increased from 1 micron at 20 layers to around 2.5 microns at 50 layers. After 50 layers per line, the width increases much more and the height does not increase as much. Further, the smoothness and consistency of the surface remains fairly stable up to 50 layers. After this, the surface finish of the depositions degrades – coinciding with the increasing width (outside the toolpath) in the XY plane. These results show that (1) the addition of multiple layers can increase the height of the structure and (2) the addition of too many layers before a sintering step can result in an increase in width rather than an increase in height of the structure. With further research, this critical number of layers before sintering can be quantified and controlled when toolpath code is compiled.
(a)
Figure 5.21: Effect of layer thickness before sintering on (a) Structure width (b) Structure height
5.9 Dynamic sintering tests

Dynamic tests were run using the same nanomaterials as the static tests discussed in chapter 3, but the ink composition was altered for use in the inkjet to avoid clogging of the nozzle. Unlike the previous tests, the hot plate was not used, with all ink drying accomplished through photonic heating only to remove any potential for a degree of necking that could potentially be caused by the elevated temperature of the hotplate. Note that the removal of the hot plate also implies that the substrate is not being preheated. The purpose of these tests was to examine the differences in the microstructure of the sintered material between the static and dynamic tests to determine the feasibility of using the system to automatically deposit and sinter nanomaterial for additive manufacturing without any substrate heating.

To drive off the water in the ink, the ink was subjected to one pass of incident light at 100% power and 0.5mm/s feedrate (8 seconds of light exposure). Despite the change in how the drying was accomplished, the morphology lines had similar mesoscale structure and dimensions to those in Figure 5.17. After the 50 layers were deposited, the structure was subject to three photonic sintering passes at the same settings for 24 total seconds of light exposure. All of the tests run in this section were with single line depositions, 50 layers thick, rather than multiple overlapped lines, to minimize operational time. Note that the microstructure of the sintered structure, as measured by SEM, was found to be unchanged between single lines and multiple overlapped lines.
The only 10nm silver ink that was available at the time of these tests was suspended in tetradecane, which was incompatible with the inkjet, so that dynamic sintering of this material could not be tested. Samples of all the other materials, however, were tested.

First, an ink consisting of 1wt% 20nm silver suspended in water was tested. The obtained microstructure of the sintered materials shown in Figure 5.22, and are very similar to the static test using 50wt% in tetradecane. Next, an ink consisting of 1wt% 20nm silver suspended in water was run, with the SEM image of the sintered material microstructure shown in Figure 5.23. Again, the results are very similar to those of the static test using 50wt% 40nm Ag in tetradecane. The AZO, ITO and WC inks also were mixed at 1wt% into water, and again yielded nearly identical sintered microstructure as in the static tests (Figs. 5.24 through 5.26). Next, 20nm and 40nm silver inks were also mixed in the same ratios that the 20 and 40nm inks were blended into 10nm ink in the early static tests to investigate if similar results would be seen when mixing the larger particle sizes. The results are shown below in Figures 5.27 through 5.30, below. It can be seen that neck growth between the nanoparticles is similar to that observed from static tests in chapter 3, indicating that it is possible to sinter the nanoparticles using photonic sintering without any preheating of the substrate. Further, densification seen in static tests is transferable to results seen in dynamic tests. Static tests in Chapter 3 have shown that particles with small diameters (e.g., less than 10nm for silver) can dramatically improve both surface finish and the degree density of the sintered structures. Further ink development is ongoing and is expected to result in a suspension that is able to flow reliably through the
inkjet and result in structures that resemble those of the static tests with 10nm Ag ink in the near future.

Figure 5.22: Ag 20nm, 1 wt% in water

Figure 5.23: Ag 40nm, 1 wt% in water
Figure 5.24: AZO 15nm, 1 wt% in water

Figure 5.25: ITO 20-70nm, 1 wt% in water
Figure 5.26: WC 55nm, 1 wt% in water

Figure 5.27: 20-40nm Ag mixed 4:1
Figure 5.28: 20-40nm Ag mixed 3:2

Figure 5.29: 20-40nm Ag mixed 2:3
5.10 Summary and Inferences

This section summarizes observations from this chapter, and discusses its implications.

**Machine design/fabrication:** The machine, as designed, has proven to be very reliable. The motion stage, light source and hot plate have been completely free of problems under heavy use for the entire course of the project. The inkjet is the most sensitive part of the system and initially had a wide variety of jetting problems that were caused both by improper ink composition and user error. After the ink is refined, however, the inkjet is essentially trouble free as long as strict startup, shutdown and operating procedures are followed (see Appendix A). With further ink development, as well as software and hardware development, the reliability of the system can be increased to the level of
polymer additive manufacturing. This can be accomplished by either releasing the
technology in an open source manner or licensing and commercializing.

**Dynamic deposition and sintering:** Using an ink with a lower loading percentage has little
measureable effect on the final structure of the sintered material as long as the thickness
of the deposition is sufficient to fully cover the substrate before sintering. However, a few
problems related to using an ink with low nanoparticle loadings were encountered. The
two main drawbacks of using a low wt% ink are:

(1) The increased amount of time required to build up the nanoparticle layer thickness –
using a 1wt% ink requires 50 layers (or inkjet passes) to reach a thickness similar to the
thickness of one layer with a 50wt% ink.

(2) The relatively low photonic heating due to the large ratio of volume of solvent to
volume of particles. Not only is the total heat generation less, but the volume of solvent
that must be flashed off is high. Using a hot plate to drive off the ink solvent is a partial
solution, but it limits the types of substrates that can be used (i.e. PLA quickly becomes
deformed when subject to elevated plate temperatures).

Despite these limitations, the prototype system can build structures of sintered silver
relatively quickly on substrates that are able to withstand the slightly elevated
temperatures required to speed up the deposition process. With the use of inkjet heads
that can deposit higher loading inks, the system can feasibly create 3-d structures on a
wide variety of substrates.
**Multi-material capability:** The test results on alternative materials in chapter 3 have shown the feasibility of sintering non-metallic nanoparticles. The prototype system has also been shown to be compatible these same materials (albeit in lower ink concentrations). Non-metallic materials share the same drawbacks as metallic inks mixed at lower concentrations – lower heat generation and large solvent volumes. Some of the non-metallic materials intrinsically have lower photonic heating which compounds the problems of solvent vaporization at low concentrations. Use of higher loading inks or hot plate use would diminish or eliminate these drawbacks, however. At the present time, constructing structures from alternative materials is feasible but is dependent on external heating in order to speed up the process.

With additional research and development in inks, hardware and software, material capability could be improved, the process made more reliable and faster, and the construction of complex multi-material 3-d structures made a reality.
Chapter 6: Conclusions and Future Work

Photonic sintering of nanoparticles is a relatively new process for sintering of nanoparticles, deposited on a substrate, into functional solid structures. The working principle of this process is the incidence of large-area broad-spectrum light onto deposited nanoparticles, which results in heat generation in the nanoparticles and their subsequent densification. Key advantages of photonic sintering include rapid, scalable and ambient condition operation. For these reasons there is significant interest in using this process as a manufacturing solution for nanoparticle sintering in emerging applications like RFID tags, flexible electronics, solar cells, and sensors. The goals of this work were as follows:

1. Experimentally characterize densification and temperature evolution in photonic sintering as a function of nanoparticle size and material type (elemental metallic vs. non-metallic compounds). (Chapter 3)

2. Computationally model and understand the nanoscale physics behind photonic sintering, use this model to qualitatively explain observed experimental trends and to examine whether current photonic sintering models adequately describe the process physics. (Chapter 4)

3. Develop a novel Xenon-Light-Additive-Manufacturing-Process (LAMP) for a low-cost, multi-material capable, desktop 3D additive manufacturing process by combining photonic sintering with inkjet deposition. (Chapter 5)
Some of the key findings and directions for future work that emerged from this project are summarized below.

1.) The sintering experiments for silver nanoparticles show that smaller nanoparticles undergo greater densification than larger nanoparticles of the same material, under the same incident power and in the same time. At the same time, the temperature rise in smaller nanoparticles is lower. The coupled multiphysical model developed in Chapter 4 is able to capture the temperature and densification trends that are seen experimentally. It further shows that since densification in photonic sintering is a competition between reduction of photonic heating due to neck growth and energy needed to cause neck growth, nanoparticle size has a significant influence on densification in the process. While smaller nanoparticles do result in lesser temperature rise, it is their ability to densify faster due to a higher surface area to volume ratio that results in a low-temperature, high-density capability. It is also observed that current models of photonic sintering are unable to capture this critical physics of the process and can therefore overestimate the optical power needed to cause densification. For example, the point during sintering when the loss of heat from the ensemble catches up with the photonic heating source is significantly underestimated by current models. Similarly, the experimental temperature trends are also not adequately captured by current models. The resultant overestimation of
required optical power can cause damage to the substrate and reduce the ability to control the microstructure of the sintered material.

2.) When sintering mixed nanoparticle inks, it is observed that the larger nanoparticles seem to be embedded in a matrix of dense material. However, the occurrence or absence of this phenomena depends on the ratio of number of smaller to larger nanoparticles. Further the temperature rise of the mixed inks during sintering falls between that of the pure nanoparticle inks – higher than the pure smaller nanoparticle ink and lower than the pure larger nanoparticle ink. The model developed in Chapter 4 also shows that mixing of nanoparticles of different sizes generates temperatures that are intermediate between pure inks of the two different nanoparticle sizes. At the same time, increasing the ratio by weight of the smaller nanoparticles to the bigger nanoparticles increases densification. This is because the larger nanoparticles act as local sources of high photonic heat generation. This heat is transferred via conduction to the smaller nanoparticles, resulting in rapid neck growth between the smaller nanoparticles, even though the neck growth between the smaller and larger nanoparticles is slower. Thus, the larger nanoparticles get embedded in a matrix of sintered smaller nanoparticles. This indicates that design of nanoparticle sizes and nanoparticle size distributions in a nanoparticle ink is a key element needed for control of sintered material density and temperature in photonic sintering.

In addition to providing an improved understanding of the physics of photonic sintering, the multiphysical model developed in this work also provides a solid
foundation in nanoscale physics of the process that is needed to quantitatively predict the mesoscale physics of the process. Future work in modeling of photonic sintering will attempt to computationally scale this process mechanics to understand how it affects sintering of a larger ensemble of deposited nanoparticles.

3.) Non-metallic nanoparticles can also be sintered using photonic sintering. The different degrees of optical response of different materials to the spectrum of xenon lamp light result in different sintering and substrate temperatures, as well as different degrees of densification. A key focus area of future work should be modeling the nano-to-meso scale physics of sintering of these non-metallic nanoparticles.

4.) The prototype additive manufacturing machine (costing was around $20K) designed to leverage the advantages of photonic sintering was shown to be capable of depositing and sintering nanoparticles in an ambient condition. It was shown that multiple materials could be deposited and sintered using this system and the effect of various toolpath planning parameters on the geometry of the formed structures was examined. One drawback of this system was that a lower concentration ink needed to be used to prevent clogging of the piezoelectric inkjet nozzle which increased the machine’s build time of sintered 3-d structures. While the use of photonic sintering for additive manufacturing has been shown here, the combination of photonic sintering with methods for depositing inks with higher loading concentrations will significantly advance the development of a commercially feasible additive manufacturing system.
Integration of the light source for full control using the same software as is used to control the motion stage and inkjet is also a key refinement that would increase the functionality of the system, allowing light to be delivered automatically and only when and at the intensity needed. This could increase lamp life by shutting down the bulb when extended periods of no light use are present in the code.

At this point, nanoparticle inks are expensive, but prices are expected to decrease, increasing the accessibility of the process. That, combined with further hardware and software development and greater understanding of the physics behind photonic sintering, could be the drivers for significant refinement of the developed additive manufacturing system. Further development and commercialization of the system developed here has the potential to increase accessibility of low-cost, multi-material additive manufacturing (metals, semi-conductors and ceramics) similar to the currently increased accessibility of polymer 3D printing.
Appendix A: LAMP operating procedures

A.1 System initialization

Before the system can be used, it must be properly initialized. The startup procedure is outlined below:

1.) Ensure the DE03, syringe pump and inspection camera are connected to the control PC and that all equipment is powered on. Open the DE03 software and wait for the software to check the connection to all the devices. If a connection error is encountered, cycle the power on the DE03 and retry. If the error persists, ensure the COM ports are assigned correctly. Successful initialization of the syringe pump and DE03 is shown below.
2.) Open the uEye software and click the live video button.

Once the main window appears, press the play button in the upper left corner to activate the side camera.
3.) Open the Motion Control window.

Click the button labeled Reset, Initialize Home All Axis to connect to the motion system.

The following lines should appear in the DE03 Syringe App window if the system initializes properly:

```
Initializing Motion Control ...
Serial Port: COM4
All Servo Boards Found, communication established
Initialize Successful
```
Next, home each axis individually by sequentially clicking the Home Z, Home Y and Home X buttons, in that order. Homing the Z-Axis first is very important to avoid collisions between the motion stage and stationary objects on the platform. A check will appear in each box after the homing procedure is completed. Occasionally, an axis will stall (usually caused by homing an axis that is already very close to the home position). The following error will be displayed:

Error 86 corresponds to a stalled motor (Axis 1 = X, Axis 2= Y, Axis 3= Z). Clicking OK and re-homing the stalled axis should correct the problem. If it does not, see Setting Motor Current, Appendix C.1. At this point the motion stage is homed, initialized and ready for use.

4.) Next, the inkjet must be prepared. Open the Syringe Control window as shown below:
Under the Valve section, select “Bypass” to complete the fluid path between the fluid reservoir and the dispense head connection.

Once the valve has finished moving, apply vacuum to the connection point of the inkjet for a sufficient time to draw degassed water the entire distance from the degasser to the connection point of the inkjet. This is done by watching the fluid velocity to estimate the time required to flush the length of the line.
When a sufficient amount of water has been drawn, remove the vacuum source and quickly click “Output” to change the valve position to prevent siphoning of the water back to the reservoir. Removing vacuum momentarily before switching the valve is important to slow the flow of water before closing the valve to prevent bubble formation in the line. With practice, it can be done without any backflow of water to the reservoir. Connect the inkjet line to the T-connector.
Once the inkjet line is securely connected, remove the small section of rubber tubing used to protect the nozzle orifice and open the recipe (File – Open) in the main software window. Press the play button to execute the sequence.

Upon execution, the User Input dialog box will appear:

Type “1” to select the option “WASH WITH SONICATE”. Enter “1” again when prompted to continue to wash point, but do not enter “1” when prompted to continue moving down. This will position the inkjet nozzle above the well assigned as the tip washing location. Next, the system must be primed to fill the inkjet with water. In the Syringe Control window, set the Speed Code to 12 if using a 67µm nozzle, or 14 for a 32µm nozzle. The volume should be set to the maximum value
of 100µl, and the number of priming cycles set to 3. Click the “Prime ->” button to begin the priming sequence.

After the sequence completes, the tip should be full of water and the well below should be filled sufficiently to allow the continuation of the wash with sonicate sequence. Enter “1” again to move the tip into the well, and “1” again to proceed to sonicate. When the sequence finishes, again enter “1” to switch the valve back to bypass.

5.) The User Input dialog box should reappear. Next, inkjet function must be checked. Use option 3 in the User Input window to view the jet using the inspection camera. When fired, the droplet pattern should be consistent:
If it is not, check the nozzle for visible bubbles or tip wetting. If either are present, refer to the operating procedures section for procedures to restore inkjet function. If the pattern looks like the above image, the system is now ready to use.

A.2 Operating procedures

Once correctly initialized, the system is fairly easy to use with the pre-written recipes. This section will consist mainly of common problems and how to correct them. The motion stage is essentially trouble free unless safe feedrates are exceeded or poor programming or homing practice results in a motion stage impact with any fixed object. The inkjet, however, is much more prone to problems resulting in poor or no jetting of inks.
The most common reasons for jetting failures are air bubbles in the line, nozzle clogging and incorrect inks. When using an ink developed for the system, bubbles are the most prevalent problem.

**Air bubbles** can be introduced into the lines in many ways, but the most common are as follows:

1.) Loose fittings – fittings can be loose enough to introduce air into the line even if no water is leaking. Evidence of loose fittings are bubbles visible slightly downstream of the fitting, often clinging to the wall of the tubing. Many times, however, bubbles cannot be seen. The symptoms include intermittent jetting failure and/or poor jetting droplet pattern. To correct, tighten all fittings (especially downstream of the degasser), and use vacuum to draw a fresh column of water from the degasser to the inkjet attachment point, and re-prime the system.

2.) Nozzle gulping air – this can be caused by shocks to the fluidics (bumping or jarring) or by excessively high motion stage acceleration. Air bubbles can usually be seen stuck inside the nozzle with the side inspection camera. Many times commanding the nozzle to wash with sonicate will clear the bubble(s). If two consecutive sonicate cycles fail to clear the bubble, stubborn bubbles can often be cleared with 1-2 priming cycles at the bottom of the wash well (so the nozzle is submerged in water) followed by a sonication cycle. Worst case, the bubble can be cleared by back flushing with methanol.
3.) Introduction of air into the lines due to improper initialization – most often air introduced during initialization is caused by changing the valve from bypass to output while vacuum is applied. Re-drawing a water column from the degasser usually solves this issue.

4.) Air bubbles in aspirated ink – similar to gulped bubbles, they can be seen in the side camera and are solved in the same manner. Care is advised when filling the wells with ink to avoid creating foam or bubbles clinging to the side of the well walls.

**Nozzle clogging** is caused by impurities in the ink, agglomerated particles, or due to particles in the ink settling over time when too large a volume of ink is aspirated. All but the toughest nozzle clogging can be cleared by washing with sonicate and/or back flushing the inkjet.

**Wetting of the tip** can also cause jetting problems. The droplet of ink or water can easily be seen in the camera or many times with the naked eye. Swabbing the tip to remove the water resolves a wetted nozzle. Inks of the incorrect formulation can cause wetting which cannot be resolved by swabbing.

**Filling the system** with anything other than distilled water may cause problems or permanent system damage if aggressive solvents are introduced. To properly refill the system with distilled water, fill the fluid reservoir, place the syringe pump in bypass mode and connect a vacuum source to the inkjet connection to draw water through the entire fluid path.
A.3 System idle

If the system will be used again in less than four hours, it can be left idle. To prepare for idle state, wash any ink away using the sonicate sequence, but do not enter “1” when prompted to switch the valve to bypass. Following this procedure will leave the nozzle filled with clean distilled water and submerged in the wash well. This will prevent deposits from forming due to evaporation from the tip which may occur if the nozzle is left idle and exposed to air for more than 5 minutes.

A.4 System shutdown

To shut the system down, option 5 should be selected in the User Input window to move the system to the safe point. The motion stage requires no further action from the user before power-down. If the inkjet will be left idle for more than 4 hours, it must be back flushed with methanol. To back flush, connect the small rubber line from the small methanol bottle to the tip of the inkjet. Then disconnect the inkjet line from the syringe pump and attach the vacuum source to the inkjet line. This will begin pulling methanol from the bottle through the tip, removing impurities and residual fluid.
Appendix B: Gantry commands and frequently used code/functions

B.1 Commands

The common commands for the system are displayed in the User Input dialog box when the system is initialized and the recipe is waiting for user input. The commands can be set and modified at the top of the recipe file. They are simply a way to command the system to jump to predetermined points in the code using the graphical user interface.

An example of the User Input dialog box is shown below:

The system response to each command is as follows:

1=**Wash with sonicate**: initiates the wash sequence to clear bubbles, clogs, unused ink or other impurities from the nozzle by forcing 100µl of distilled water through the nozzle orifice while exciting the piezoelectric element at various frequencies to loosen stuck particles.

2=**Aspirate sample**: draws a sample into the nozzle from the sample well and in the volume specified in the code.
3= **Inspect side cam**: moves the nozzle into the camera’s field of view for inspection of the nozzle and jetting pattern.

4= **Dispense line**: deposits a single line onto the target.

5= **Move safe**: moves the motion system to the safe point for manual maintenance, shutdown or short term idle state.

6= **Sinter grid**: moves the distal end of the light source over the target area. Using the current revision of the software, the light source must be turned on manually by using the buttons on the light source, or by manually initiating a script using the terminal software.

7= **Film and sinter**: Fully automated routine with multiple sample draws and deposition sequences followed by a sintering pass. This is the primary function of the recipe.

Each of the functions described above vary slightly from recipe to recipe and can be customized by the user in the code. The number of functions that can be called from the User Input dialog box is not inherently limited.

**B.2 Programming procedures**

The system is programmed by adding or modifying commands. Commands 1, 2, 3 and 5 should not be modified except by an expert user – they are critical to correct system operation.

At this stage in the software development, points which the system moves to must be pre-declared in order to be used in the software. Planned revisions to the software
include the capability to read points directly from the code, or import G-Code from external files.

**Declaring points:** points can be declared in the file in the following format:

```c
DEFINE_POINT(VariableName=SAFE_PT,
    X=0.0,
    Y=100.0,
    Z=0.0)
```

Where “SAFE_PT” is the variable name, followed by the coordinates.

**Declaring grids:** a grid of points can be declared in the CommonPoints.txt file in the following format:

```c
DEFINE_GRID(VariableName=MICROPLATE_T1_GR,
    X=119.4,
    Y=143.5,
    Z=-28,
    XSteps=12,
    XIncrement=9.0,
    YSteps=8,
    YIncrement=-9.0)
```

Where “MICROPLATE_T1_GR” is the variable name, followed by the coordinates of point (0,0). Xsteps is the number of points in the grid in the X-direction, XIncrement is the distance between the points in mm. Likewise for Y. Points in the grid can be called in the program using the following syntax: `<variable name> [X,Y], where `<variable name>` is
replaced by the name of the declared variable and X and Y are the point numbers in X and Y, respectively. See the motion section for examples.

**Motion:**

Motion can be commanded in the code using the MOVE_TO_POINT command in the following format:

```plaintext
MOVE_TO_POINT(Tool=SYSTEM_TIP1, Point=TARGET_T1_GR[0,0], Speed_pct=50, MoveToSafeHeightFirst=TRUE)
```

This example is moving the nozzle to point [0,0] of the grid declared by TARGET_T1_GR. A move to a point can be called by leaving off the [0,0]. Speed_pct is the percentage of full axis speed as declared in CommonVariables.txt. Setting MoveToSafeHeightFirst to TRUE or FALSE will determine whether the system will move the Z-Axis up to the clearance plane before executing the move. Setting this to TRUE is highly recommended for non-expert users.

**Inkjet drive:** The inkjet is driven by the following piece of code:

```plaintext
DE03_STOP_WAVEFORM()

DE03_COS_SETUP(Tip=1, DesiredFreq=13000, InBurstNo=250, CosAmplitude=2000)
```
StrobeDuration=1, 
StrobeDelay=0, 
NumOfBursts=1, 
TriggerSetting=0, 
TriggerDelay=100, 
TriggerPeriod=1)

DE03_START_WAVEFORM(WaitForCompletion=FALSE, 
Timeout_ms=1000)

The deposition can be adjusted in the following manner:

DesiredFreq sets the frequency of the excitation wave driving the piezoelectric element in the inkjet and thus the frequency of droplet generation.

InBurstNo sets the number of droplets in the burst

CosAmplitude sets the excitation amplitude (range from 0-2047)

TriggerSetting sets whether the system waits for an external trigger to begin droplet generation. If set to zero, the droplet generation begins immediately. If set to 1, the generation begins when the DE03 input pin is triggered high (in the case of this system that occurs when the optical trigger switch is “closed” or the beam is first obstructed – the trigger activates on the leading edge of the switch blade). If set to 2, the generation begins when the input pin is pulled low after being pulled high (or the optical switch is “open” after being closed – the trigger activated on the trailing edge of the switch blade).
B.3 Modifying software parameters

System operating parameters can be changed by adjusting the variables in the referenced file. The variable files are listed below with a description of the parameters that the user can change within them. **To avoid system damage or poor system performance, variables should not be modified without consulting with an expert on the system.**

The file CommonVariables.txt contains set points for axis velocities and accelerations, as well as other declared variables to reduce code bloat in recipe files. Modification of these values can result in improper feedrates in recipes (all feedrates are referenced to these set values) or motor stalling if set in the wrong range.

The file CommonPoints.txt contains all the point location data for automated system movement. Improper modification of these values by the user can result in severe system damage.

For further information on the system, refer to the operating manual provided with the Engineering Arts software, Hamilton syringe pump and Schneider electric motors or consult an expert on the system.
Appendix C: Technical system details and schematics

C.1 Motion system:

Power Requirements: The motion stage requires 48v power to be supplied to each motor using a dedicated cable – chaining of power supply cables can cause inconsistent motor performance. The power supply specified for this application is a Cosel PLA600F-48, which can supply 12.5 A at 48V. (Each motor draws approximately 2A at maximum, for a total of 6A). A decoupling capacitor should be placed across the positive and negative lines at each motor’s power connection (be mindful of electrolytic capacitor polarity when connecting!)

The motors also require a 24v power source for backup in case of failure of main power to preserve volatile memory, but the power requirements are minimal, so no specific supply is specified.

Ensure the shielding in the power and communication cables as well as the motor bodies are connected to the earth ground of the power supply. For more information on power and ground requirements, or before making any changes to the system, refer to chapter 5 of the LexiumMDrive Motion Control NEMA 17/42mm Hardware Manual, V1.00, 08/2014.

Motor and home switch wiring: all necessary information for wiring of the motors and home switches is presented in this section. Schematics for custom boards and wiring guides are given. In addition, excerpts from Chapter 6 of the LexiumMDrive Motion Control NEMA 17/42mm Hardware Manual and The LexiumMDrive Motion Control Quick
Reference are also provided to aid in identifying pinouts of the motors, as well as diagnosing problems with wiring.

The custom board has the following schematic:

Pinouts on the motor in and motor out start with pin1 on the left and end with pin 8 on the right. The cabling should be connected to the board in the following manner:

<table>
<thead>
<tr>
<th>Function</th>
<th>Motor In</th>
<th>Motor Out</th>
<th>DB 9 (female on board)</th>
<th>DB 9 (male on 1st unit cable)</th>
<th>Wire Color in cable</th>
<th>Optional 120 resistor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aux GND</td>
<td>Pin 1</td>
<td>Pin 1</td>
<td>NC</td>
<td>NC</td>
<td>Red / White</td>
<td>R1 (for 1st in series)</td>
</tr>
<tr>
<td>Aux +24V</td>
<td>Pin 2</td>
<td>Pin 2</td>
<td>NC</td>
<td>NC</td>
<td>Red</td>
<td>R1 (for first in series)</td>
</tr>
<tr>
<td>Comm GND</td>
<td>Pin 3</td>
<td>Pin 3</td>
<td>Pin 6</td>
<td>Pin 6</td>
<td>Blk / white</td>
<td>R2 (for last in series)</td>
</tr>
<tr>
<td>Comm GND</td>
<td>Pin 4</td>
<td>Pin 4</td>
<td>Pin 4</td>
<td>Pin 4</td>
<td>Blk</td>
<td></td>
</tr>
<tr>
<td>RX-</td>
<td>Pin 5</td>
<td>Pin 5</td>
<td>Pin 2</td>
<td>Pin 2</td>
<td>Yel</td>
<td>R1 (for 1st in series)</td>
</tr>
<tr>
<td>RX+</td>
<td>Pin 6</td>
<td>Pin 6</td>
<td>Pin 7</td>
<td>Pin 7</td>
<td>Yel / White</td>
<td>R1 (for first in series)</td>
</tr>
<tr>
<td>TX+</td>
<td>Pin 7</td>
<td>Pin 7</td>
<td>Pin 3</td>
<td>Pin 3</td>
<td>Grn / White</td>
<td>R2 (for last in series)</td>
</tr>
<tr>
<td>TX-</td>
<td>Pin 8</td>
<td>Pin 8</td>
<td>Pin 8</td>
<td>Pin 8</td>
<td>Grn</td>
<td>R2 (for last in series)</td>
</tr>
</tbody>
</table>
The pinouts for the connections on the motor body are shown below:

<table>
<thead>
<tr>
<th>Connector</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Supply voltage VDC</td>
</tr>
<tr>
<td>P2</td>
<td>Multifunction interface</td>
</tr>
<tr>
<td>P3</td>
<td>Service interface</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pin</th>
<th>Signal</th>
<th>Function</th>
<th>I/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>INPUT REFERENCE</td>
<td>Bias the input as sinking or sourcing</td>
<td>—</td>
</tr>
<tr>
<td>2a</td>
<td>N/C</td>
<td>Not connected</td>
<td>I</td>
</tr>
<tr>
<td>3a</td>
<td>IN2</td>
<td>General purpose programmable input 2.</td>
<td>I</td>
</tr>
<tr>
<td>4a</td>
<td>IN3</td>
<td>General purpose programmable input 3.</td>
<td>I</td>
</tr>
<tr>
<td>5a</td>
<td>IN4</td>
<td>General purpose programmable input 4.</td>
<td>I</td>
</tr>
<tr>
<td>6a</td>
<td>ANALOG_IN</td>
<td>Analog Input</td>
<td>I</td>
</tr>
<tr>
<td>7a</td>
<td>LOGIC_GND</td>
<td>Logic ground (non-isolated)</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pin</th>
<th>Signal</th>
<th>Function</th>
<th>I/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>AUX_PWR</td>
<td>0...24V auxiliary power input maintains logic circuitry and position information in the event of SUPPLY VOLTAGE VDC power loss.</td>
<td>—</td>
</tr>
<tr>
<td>2b</td>
<td>N/C</td>
<td>Not connected</td>
<td>O</td>
</tr>
<tr>
<td>3b</td>
<td>N/C</td>
<td>Not connected</td>
<td>O</td>
</tr>
<tr>
<td>4b</td>
<td>N/C</td>
<td>Not connected</td>
<td>O</td>
</tr>
<tr>
<td>5b</td>
<td>N/C</td>
<td>Not connected</td>
<td>O</td>
</tr>
<tr>
<td>6b</td>
<td>SIGNAL_OUTPUT_</td>
<td>High speed signal output collector</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>COLLECTOR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7b</td>
<td>SIGNAL_OUTPUT_</td>
<td>High speed trip output emitter</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>EMITTER</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The optical home sensor is wired in the following manner:
Brown: +24v terminal block on custom motor board
White: P2 3a
Blue: ground terminal block on custom motor board
Black: not used

The completed wiring on one motor is shown below:
**Setting motors to party mode:** During the system build, before the system was functional, the motors were individually programmed to be compatible with the DE03 control. This section covers the basics of programming individual motors using the Motion Control Programmer that is installed with the LexiumMDrive Software Suite (which can be obtained from the Schneider Electric website). This required connecting to each motor individually using the cable sourced from Schneider. The details of how to set to party mode will be useful should the motors lose the settings stored in RAM, or if a motor must be replaced in the future. To set a motor to party mode for use in the motion stage, follow the following procedure:

Before beginning, please note that: Out of the box, the motor is by default not set to party mode communication. Under default settings, commands sent to the motor are terminated with CR (0D) and the response is CR LF (0D 0A). Additionally, when using default settings the commands are echoed (EM=0) as each character is typed.

1.) Type DN="n" (n= axis number, from 1 to 3– you need the quotes!). Hit enter to send the command. This names the axis whatever you put in quotes. In this system, X=1, Y=2, Z=3.
2.) Next, type EM=1, enter. This changes the echo mode – from this point, nothing you type will be echoed (you will not see anything appearing in the terminal window as you type), leading many users to assume the commands are not being sent to the motors. They are, so type carefully and exactly.
3.) Type PY=1, enter. This places the motors in party mode. In party mode, commands must be followed and terminated with CTRL+J.
4.) Send <CTRL+J> “\000A” <CTRL+J>
5.) Finally, save the settings by typing NS <CTRL+J> (N is the axis number). This command saves settings to nonvolatile memory.

**Commands in party mode:**
From this point, to communicate with the device you must, at start up, send `<CTRL+J>`. All subsequent commands must be structured in the following manner: `<CTRL+J> N <command><CTRL+J>` with N being the axis number. To communicate with all the motors at once, type `*` in place of the axis number and all motors will answer. This is convenient if you don’t know the address of a unit and want to reconfigure.

So as an example, if you wanted to command the Y-axis motor to print its serial number, you would type: `<CTRL+J> 2 PR SN<CTRL+J>` and the motor would respond with the serial number. For detailed information on commands, please reference chapters 4-7 of the MCode Programming and Software for LexiumMDrive (V 1.00, 08.2014 at the writing of this document). Note: when using the Send Command section of the Motion Control in the DE03 software, the commands do not need to be preceded or terminated by `<CTRL+J>`, and the axis number will be set using the dialog box.

**Setting motor current:** To set the software current limit in the motor controllers, send the following commands to your motors into the Send Command box that can be found in the Motion Control window. This process must be repeated for all three axes. If axis stalls are occurring frequently, checking the motor current is the first place to start.

PR RC (This will print out what percentage of max run current the motor is currently set at – if 75 is returned, no further action is necessary, if something other than 75 is returned, proceed)

RC 75 (sets the current limit to 75% of maximum – provides adequate torque while not straining the motors)

ES 2 (The default setting is ES 1, When set to ES 2, all the motors will respond to CNTR+E to stop in party mode)
S (save in non-volatile RAM.)

**Trigger switch wiring:** In order to have a consistent start of deposition, a trigger switch was installed and wired such that closing the switch would result in a +5v signal being sent to the trigger input (TTL) on the DE03 (pin 2 on the P1 DB9 connector used for strobe and I/O). The brown wire from the optical switch was connected to +5v (pin 8), the blue wire is connected to ground, and the white wire is connected to pin 2. A 10k resistor bridges pin 2 and pin 8 (brown and white wires from the switch). The pinouts are shown below, as well as a schematic for the wiring:

<table>
<thead>
<tr>
<th>Pin</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Strobe Out (TTL)</td>
</tr>
<tr>
<td>2</td>
<td><strong>Trigger Input (TTL)</strong></td>
</tr>
<tr>
<td>3</td>
<td>Sync Out (TTL)</td>
</tr>
<tr>
<td>4</td>
<td>Strobe Out High Current (Sinking Max 1 Amp, 39 Volts)</td>
</tr>
<tr>
<td>5</td>
<td>Strobe Light Power Source (IKE 2W Resistor pulled up to 24 Volts)</td>
</tr>
<tr>
<td>6</td>
<td>“On” Indicator Out (TTL)</td>
</tr>
<tr>
<td>7</td>
<td>“Status” Indicator Out (TTL)</td>
</tr>
<tr>
<td>8</td>
<td>+5V (out)</td>
</tr>
</tbody>
</table>
C.2 Light source

Scripting: using the program Terminal, the light source can be programmed using serial command scripting to perform functions for precise control of the static sintering process. Below is an example program, used to conduct sintering on deposited nanoparticle bearing ink in the static setup:

Sample Script:

//****************************
// Terminal Script
program lampcontrol;

var command: string;

begin

// Status and lamp ignition
comsendstr('S'+#13);
Delay(5000);
comsendstr('I'+#13);
Delay(5000);

// Position sample
comsendstr('M30'+#13);
Delay(500)
comsendstr('M15'+#13);
Delay(10000)
// Sinter sample for 10 seconds at 100% power
comsendstr('M250'+#13);
Delay(7000)

// Close the Aperture
comsendstr('C'+#13);
Delay(500)
comsendstr('S'+#13);

end.
C.3 Hot plate operation and technical details

The hot plate is made from off the shelf components and is totally automatic. Temperature set points are done in software by changing the declared value of the int temptarget variable. In the program below, the temperature is set to 120°C.

To provide temperature control, the controller reads the value of a 100k thermistor mounted to the hot plate surface and calculates the temperature. It then compares this temperature to the target temperature. If the plate temperature is below the target, the controller triggers relay 1 by outputting LOW (ground) on pin 8. The relay closes and energizes the heating circuit of the plate. When temperature reaches the target temperature, the pin is returned to HIGH and the relay opens, cutting off power to the plate. In this way, the plate temperature is controlled within +/- 1°C.

The plate is controlled by an Arduino microcontroller and is programmed in the Arduino flavor of C. For more information on programming an Arduino controller, please visit the Arduino Language Reference page at: http://www.arduino.cc/en/Reference/HomePage

Hot Plate Program:

// include the library code:
#include <LiquidCrystal.h>

// which analog pin to connect
#define THERMISTORPIN A0

// resistance at 25 degrees C
#define THERMISTORNOMINAL 100000

// temp. for nominal resistance (almost always 25 C)
#define TEMPERATURENOMINAL 25
// how many samples to take and average, more takes longer
// but is more 'smooth'
#define NUMSAMPLES 20
// The beta coefficient of the thermistor (usually 3000-4000)
#define BCOEFFICIENT 4066
// the value of the 'other' resistor
#define SERIESRESISTOR 100000

// initialize the library with the numbers of the interface pins
LiquidCrystallcd(12, 11, 5, 4, 3, 2);
int relay1 = 8;
int relay2 = 9;

//SET PLATE TEMPERATURE
int temptarget=120;
int samples[NUMSAMPLES];
float BB=(temptarget-0.5);
float TB=(temptarget+0.5);

void setup() {
    //Serial.begin(9600);
pinMode(relay1, OUTPUT); //Set Pin8 as output
pinMode(relay2, OUTPUT); //Set Pin9 as output
    // set up the LCD's number of columns and rows:
lcd.begin(16, 2);
    // Print a message to the LCD.
lcd.print("HOT PLATE STATUS");
digitalWrite(relay1, HIGH); //Turn off heat relay
digitalWrite(relay2, HIGH); //Turn off heat relay
}

void loop() {
  //BED THERMISTER TEMPERATURE READING
  uint8_t_i;
  float average;

  // take N samples in a row, with a slight delay
  for (i=0; i< NUMSAMPLES; i++) {
    samples[i] = analogRead(THERMISTORPIN);
    delay(10);
  }

  // average all the samples
  average = 0;
  for (i=0; i< NUMSAMPLES; i++) {
    average += samples[i];
  }
  average /= NUMSAMPLES;

  // convert the value to resistance
  average = 1023 / average - 1;
  average = SERIESRESISTOR / average;

  float temp;
  temp = average / THERMISTORNOMINAL;     // (R/Ro)
temp = log(temp); // ln(R/Ro)
temp /= BCOEFFICIENT; // 1/B * ln(R/Ro)
temp += 1.0 / (TEMPERATURENOMINAL + 273.15); // + (1/To)
temp = 1.0 / temp; // Invert

temp -= 273.15; // convert to C

if (temp < BB)
{
  digitalWrite(relay1, LOW); // Turn on heat relay
  lcd.setCursor(0, 1); // set screen print to line 2
  lcd.print("T");
  lcd.print(temp, 0);
  lcd.print("/");
  lcd.print(temptarget);
  lcd.print("C ");
  lcd.print("HEAT ON ");
}
else if (temp > TB)
{
  digitalWrite(relay1, HIGH); // Turn off heat relay
  lcd.setCursor(0, 1); // set screen print to line 2
  lcd.print("T");
  lcd.print(temp, 0);
  lcd.print("/");
  lcd.print(temptarget);
  lcd.print("C ");
  lcd.print("HEAT OFF");
}
delay (100);
}

**Hot plate wiring:**

![Hot plate wiring diagram](image)

Other pins used in the hot plate:

**Pin 8: Relay 1:** controls applied 12v to hot plate

**Pin 9: Relay 2:** connected, but unused

Both relays are ground triggered. Setting the pin to HIGH opens the relay, setting the pin to LOW closes the relay.
Pin A0: thermistor analog input reads voltage between the thermistor and the 100k resistor (a simple voltage divider).

**Appendix D: System problems encountered and overcome**

Other than ink consistency issues causing jetting problems, several problems were encountered and overcome during system development. The problems and the solution to those problems are listed in the following section.

**Overheating of the fiber optic cable:** For the prototype system, all the custom brackets were made from PLA for increased stiffness offered over ABS. Since the machine operates in conditions well below the glass transition temperature (Tg) of PLA (60-65°C), this is an acceptable material. When the hot plate was used to dry the ink, no problems were encountered – The heating of the cable threads from short bursts of light used for sintering of the material was minimal. When another program was developed in which the hot plate was not used but instead the light source was used to drive off the solvent in the ink, the light guide mount softened due to heating of the threaded end of the light guide from running the light for long periods of time. The problem was partially alleviated by removing the particles that had accumulated on the end of the fiber optic bundle, but the light guide mount still softened enough to distort over the course of a 20 minute deposition program. The solution was to rebuild the mount in ABS plastic which has a Tg of 105°C.
**Lack of space to slant the fiber optic cable:** The initial design of the system had the light guide pointing in at an angle. A problem that was not anticipated with this design was the interference with the well plate when drawing samples or washing the nozzle. The initial solution was to thin the side of the well plate using a band saw and program the system to only use the wells adjacent to the thinned side. The thinned plate was not a good permanent solution, however, as cutting weakened one of the mounting points and required extensive cleanup of plastic dust after cutting to avoid contamination or nozzle clogging. The second problem was that scattered light from the angled guide was incident on the glass inkjet nozzle, which could potentially cause jetting problems and/or damage to the nozzle. These problems, combined with the finding that the 1% ink did not dry as quickly as anticipated when exposed to light, resulted in a redesign which replaced the angled mount with an offset vertical mount. This arrangement made it possible to access the well plate while it also avoided incident light on the nozzle and allowed the distance between the fiber optic bundle end and the substrate to be smaller (for increased incident light intensity on the sample).

For fast deposition, the hot plate was used to dry the ink, which also solved the previous problems.

**Ink puddles at the beginning of the line:** When depositing lines for the first series of tests, the problem of ink forming puddles at the beginning of the deposition path was encountered. It was determined that this was caused by the gantry having to accelerate up to full speed while the inkjet was firing. Due to an oversight in the software
programming, there was no way to accelerate the gantry to full speed before starting the deposition – the software leaves no option move onto the next line of code before a move is complete. In light of this shortfall, the solution was to use the triggering function that puts the jetting command on hold until a trigger is seen on the input pin (see trigger switch wiring, Appendix C.1). The switch was placed in a location on the X-axis that would result in deposition starting when the gantry was at full speed and over the target area on the substrate. Further revisions of the software should provide the means to start and stop deposition at precise coordinates and when the gantry is moving at the feedrate required for consistent deposition.
References

[22] U. National Center for III-V technologies, (June 2012).
[73] Z. Fang, Y.-R. Zhen, O. Neumann, A. Polman, F.J. García de Abajo, P. Nordlander, N.J. Halas, Nano Letters, 13 (2013) 1736-1742.