Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information: Additive Manufacturing of Germanium Structures for Flexible Optoelectronics

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Materials and Methods

Materials: Germanium (IV) chloride, ($GeCl_4$ 99 %), nickel (II) chloride, ($NiCl_2$, 99%), thiophenol, (TP, ≥99%), sodium borohydride, ($NaBH_4$, >96%), silver nitrate, ($AgNO_3$, ≥99%), (3-Aminopropyl)triethoxysilane, (APTES, ≥98%) toluene (Reagent grade), dichloromethane (DCM-HPLC grade) ethanol, (EtOH, Reagent grade) acetonitrile, (MeCN, HPLC grade) and methanol, (MeOH, HPLC grade) were purchased from Sigma Aldrich and used without further purification.

Synthesis of Ge Nanoparticles

In a typical synthesis, 0.46 mmol $GeCl_4$ was added to 5 mL EtOH in a 20 mL vial and allowed to stir. In a separate vial, 2 mmol of $NaBH_4$ was added to 7 mL EtOH and sonicated for 45 minute. After 45 minutes 0.6 mmol TP was added to the $NaBH_4$ solution and the solution immediately added to the vial containing $GeCl_4$. The reaction was allowed to stir for 1 hour before precipitating twice with EtOH and three additional washings with MeOH. The resulting nanoparticles were dispersed in either DCM or toluene for characterization.

Synthesis of Ni Doped Ge Nanoparticles

In a typical synthesis 0.46 mmol $GeCl_4$ was added to 5 mL EtOH in a 20 mL vial. In a separate vial, 2 mmol of $NaBH_4$ was added to 7 mL EtOH and sonicated for 45 minute. After 45 minutes 0.6 mmol TP was added to the $NaBH_4$ solution and the 5 mL of the solution immediately added to the vial containing $GeCl_4$. In a third vial, an appropriate amount of MCl_2 (depending on desired dopant content) was dissolved in minimal amount EtOH. The reaction was allowed to stir for 15 minutes before adding the MCl_2 solution and remaining 2 mL of $NaBH_4$/TP. The reaction was then stirred for an additional hour before precipitating twice with EtOH and three additional washings with MeOH. The resulting NPs were dispersed in either DCM or toluene for characterization.

Synthesis of Ag-APTES-Ge Decorated Structures

In a plastic vial, 1.5 mmol $AgNO_3$ was dissolved in 5 mL of 1:4 EtOH: MeCN. In a separate glass vial, 2 mmol NaBH4 was dissolved in 5 mL EtOH and sonicated for 45 minutes. At this time, 3 mmol APTES was added to the vial and the NaBH4/APTES solution was added to the vial containing $AgNO_3$. This resulted in an immediate color change to black. The reaction was allowed to stir for 30 minutes before 15 mL of additional EtOH was added and the solution centrifuged at 5000 RPM for 10 minutes. The black solid was collected, dissolved in a minimal amount of EtOH and subsequently washed 2x's with 10 mL MeOH and 2x's with 10 mL of a 1:1 MeOH:MeCN mixture to removed excess salts and APTES. The final product, Ag-APTES nanoparticles, were dissolved in 1 mL of MeCN to be used in the next step of the synthesis. Separately, 0.46 mmol of GeCl4 was added to 5 mL of a 1:4 EtOH:MeCN and allowed to stir. In a separate vial 2 mmol NaBH4 was added to 5 mL EtOH and sonicated for 45 minutes. At this time, the NaBH4 solution was added to the GeCl4 and allowed to stir. After 10 minutes the 1.5 mL of Ag-APTES nanoparticles were added and reaction allowed to stir for an additional 30 minutes. The resulting Ag-APTES-Ge decorated structures were purified according to the procedure used previously on the Ag-APTES nanoparticles.

Printing of Ge-Based Iinks

All traces were inkjet printed by a Optomec Aerosol Jet printer which equipped with a 100 micron nozzle. Our formulated inks were printed on different substrates, including glass, silicon and kapton. All substrates, were cleaned by ethanol and acetone followed by plasma treatment for 5 min.

Optical Characterization

UV-vis absorption and photoluminescence characterization was collected using a CRAIC UV-vis NIR microspectrophotometer with samples drop casted on a glass slide. The spectra were collected from 1600-200 nm. Raman spectra were collected using a Renisaw inVia Raman microscope. Dilute solutions of NPs were drop casted onto glass slides. All Raman data was processed using inVia Wire software.

Structural Characterization

X-Ray Diffraction Patterns were obtained using a Rigaku Smartlab X-ray diffractometer. All samples were prepared by spin coating samples of the Ge NPs dissolved in toluene onto glass slides.

Scanning Tunneling Electron Microscopy (STEM)

Scanning transmission electron microscopy images were obtained using a FEI Talos F200X with a voltage of 200kV. Samples were prepared by dropping 10 μL of NPs dissolved in DCM on a 200 mesh carbon-coated copper grid (molybdenum-coated grid used for analysis of copper doped Ge NPs). The sample was allowed to set for 1 minute before any excess solution was removed by wicking with a piece of filter paper.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy images were obtained using a Zeiss Gemini 500 SEM with a voltage of 1.5 kV. All samples were prepared by spin coating diluted samples of the Ge NPs dissolved in DCM onto silicon wafers

Conductivity Measurements

Printed traces of all three Ge NP based inks both pre and post processing (thermal annealing or photonic sintering) were analyzed using a Keithley semiconductor characterization system. The probe station was used to measure current-voltage characteristics of three thin film samples for each of the different doped NPs. Three measurements were taken for each film and the average conductivity calculated using average of the nine resistivity measurements. For thermal annealing, purified solutions of the doped and undoped NPs were spin coated onto glass slides. The slides were then placed in a 350°C vacuum oven for 6 hours. For photonic sintering, a Novacemtrix PulseForge 1300 with the following conditions; 400 V, envelope 5000 μs, 20 μpulses, duty cycle at 20%, and 3 replicates. The effect of excitation wavelength on the photorepsonse of the conductivity was investigated using 5 different light sources each having the same operating power of 30 mW at wavelengths of 360, 450, 532, 650 and 785 nm respectively,

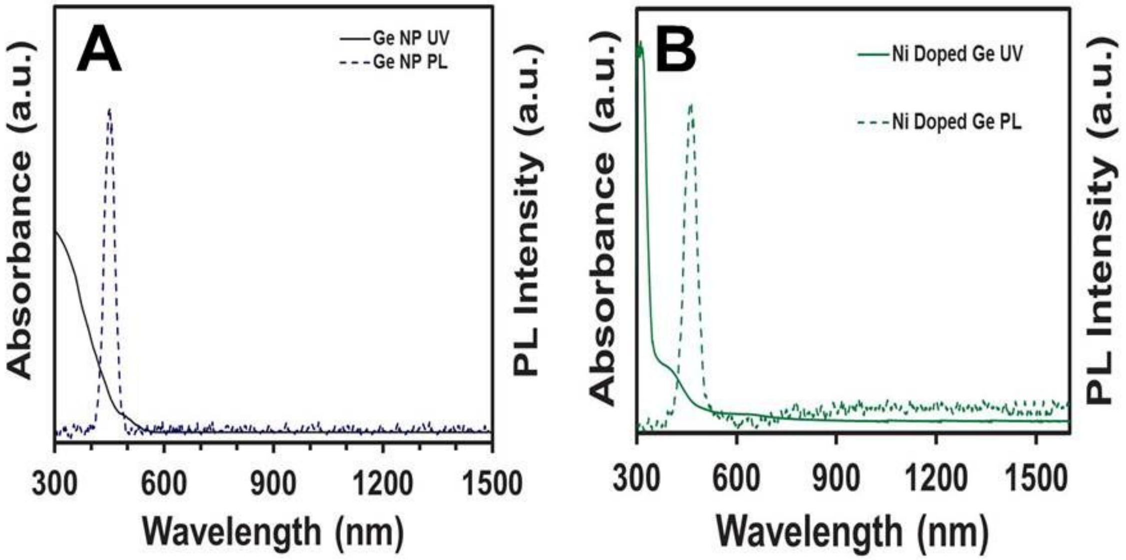


Figure SI1: Absorption and emission spectra of pristine Ge NP ink (A) and Ni doped Ge NP based ink (B).

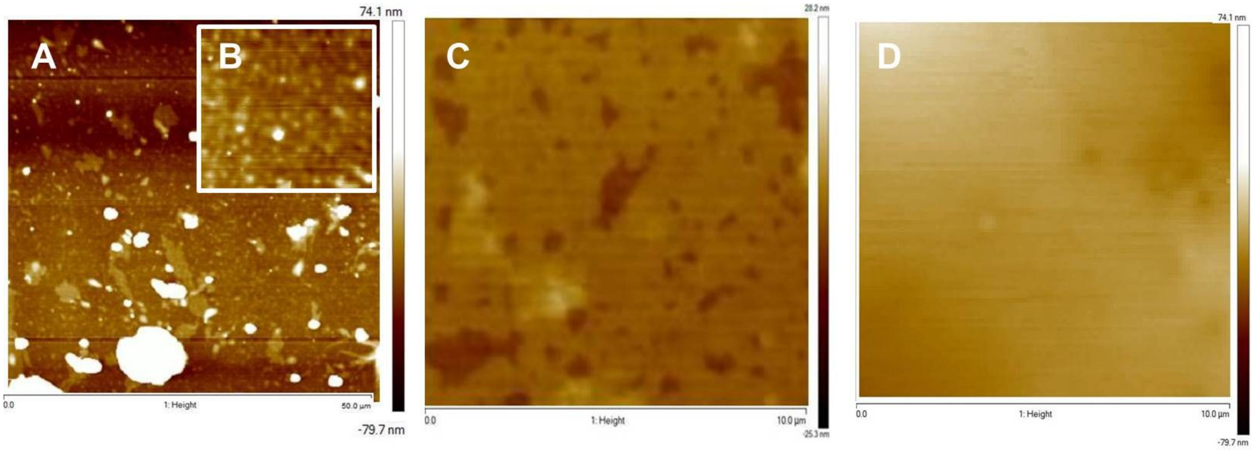


Figure SI2: AFM images corresponding to line scans of pristine Ge NP based ink as printed (A and B (area of 10 μm)), after thermal annealing (C), and after photonic sintering (D).

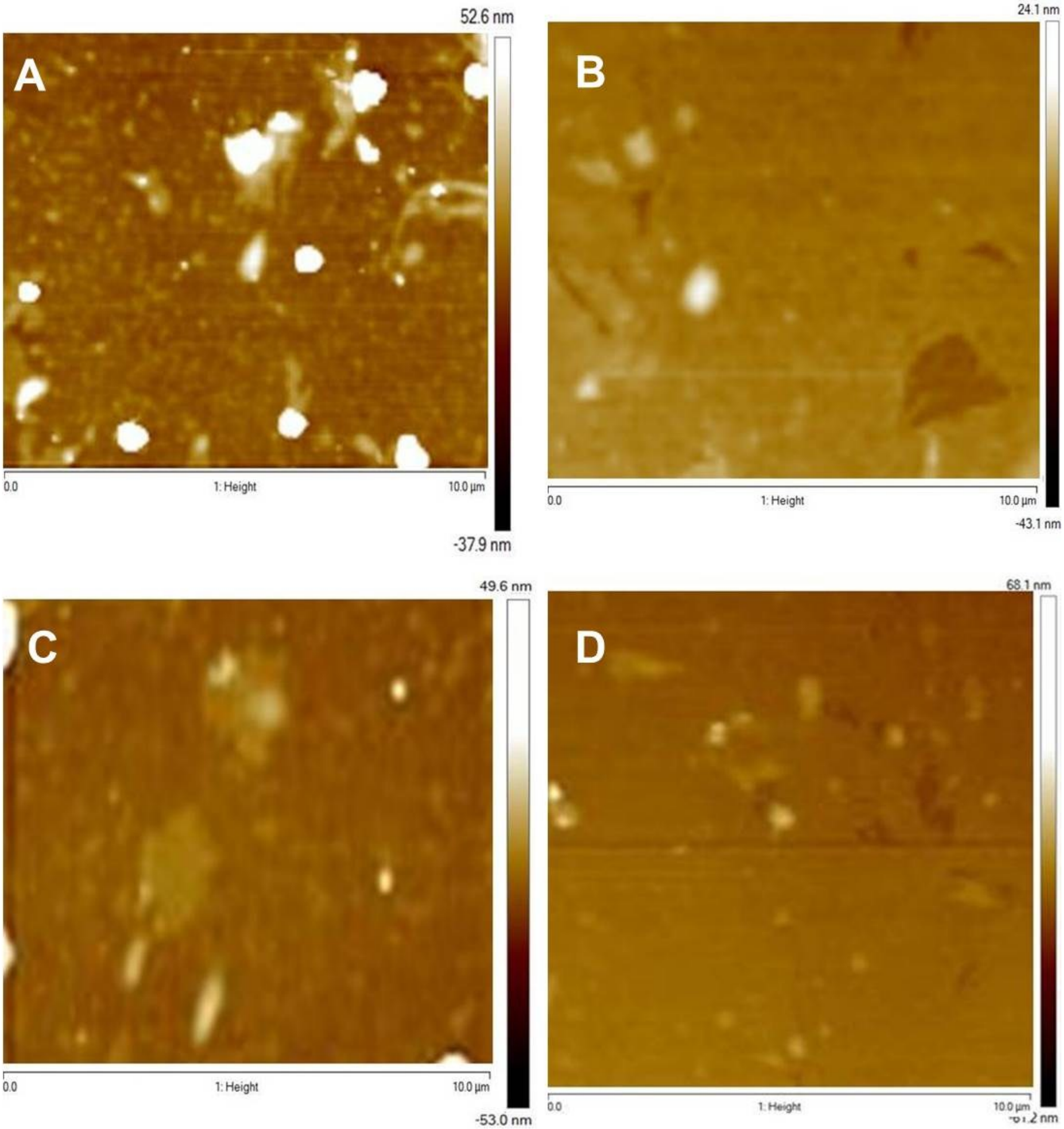


Figure SI3: AFM images corresponding to line scans of Ni doped Ge NP based ink as printed (A) and after photonic sintering (B) as well as Ag-decorated Ge hybrid structure based ink as prited (C) and after photonic sintering (D).

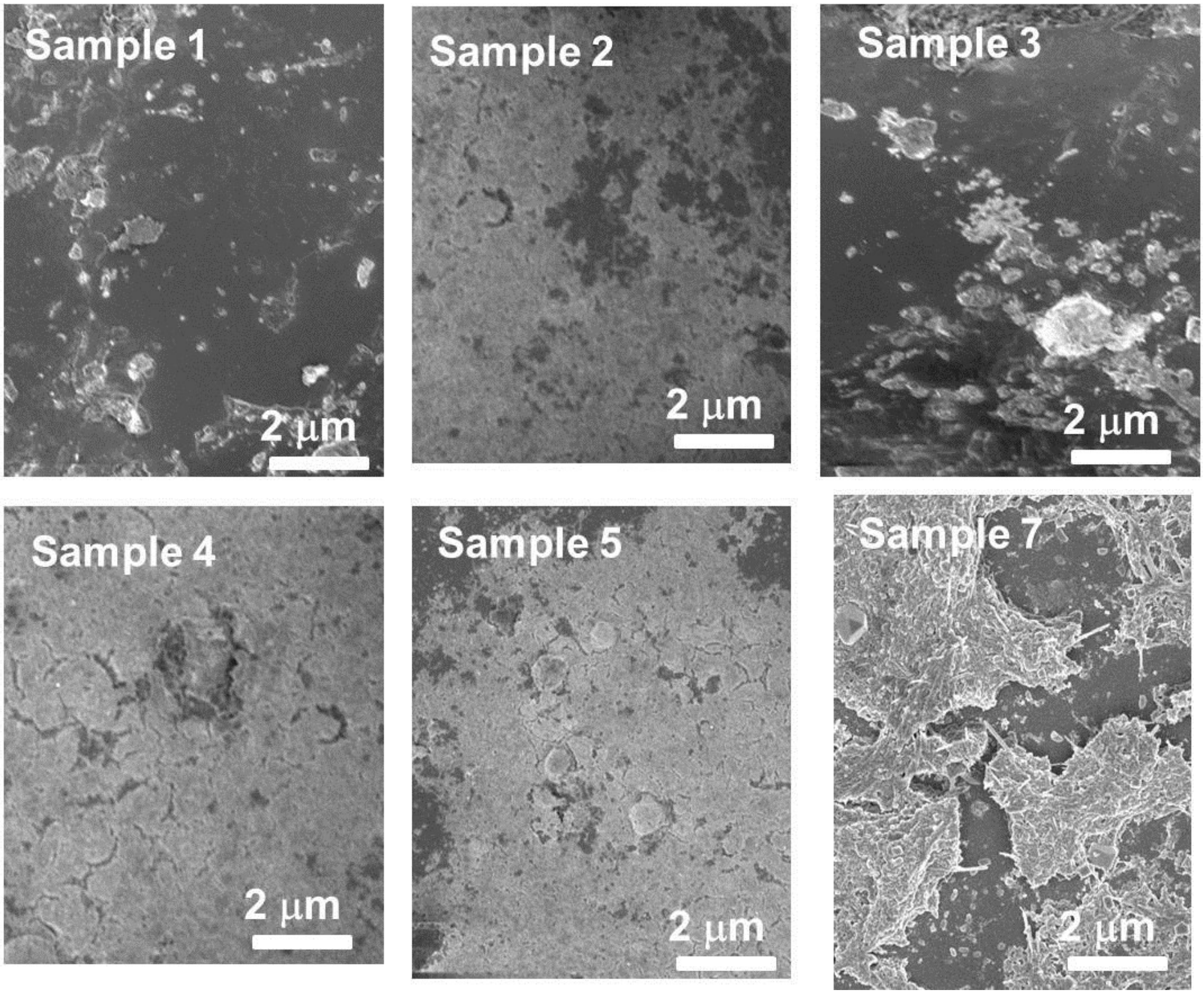


Figure SI4: SEM images of pristine Ge NP based ink after photonic sintering with various conditions described in Table S5. (Sample 6 is excluded since it was determined to be optimal and images showing film quality are included in the manuscript

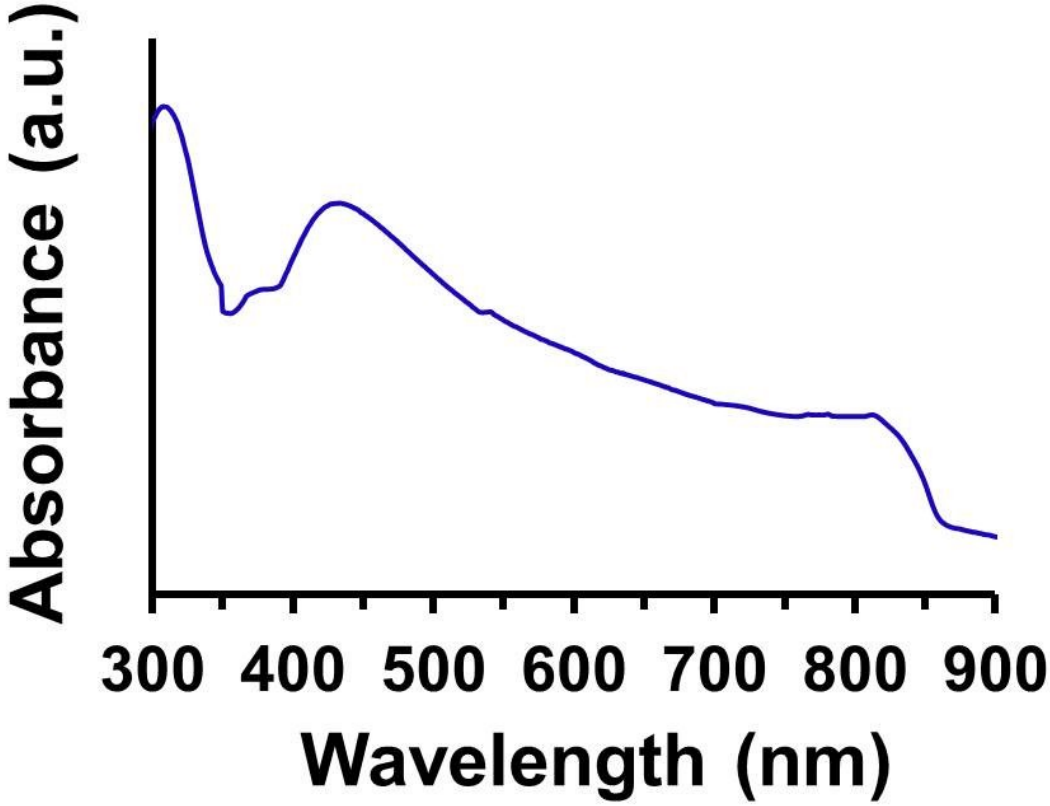
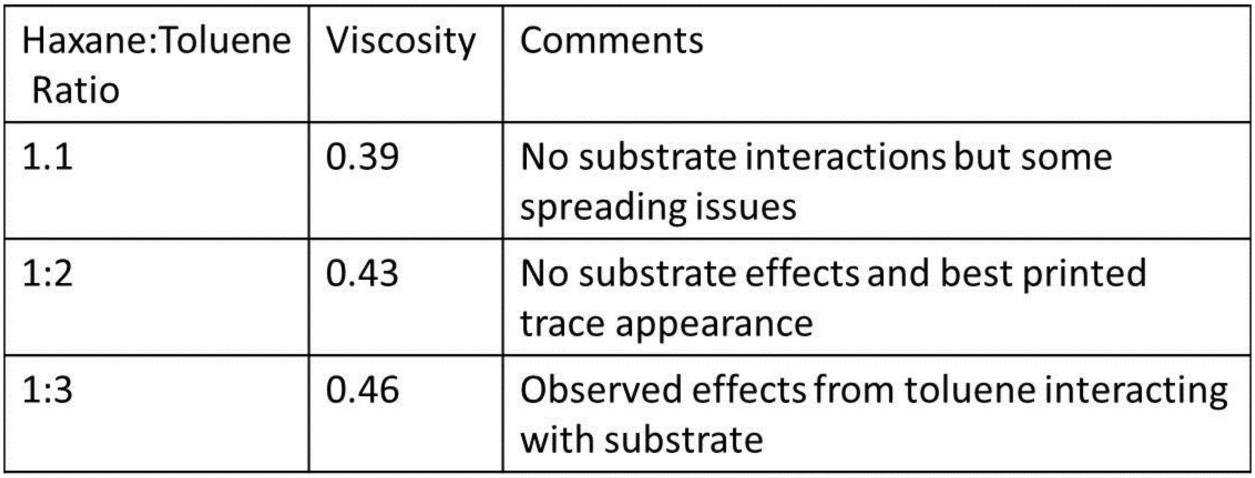


Figure SI1: Absorption spectra of sintered Ag decorated Ge NP ink. Peak broadening is consistent with previous reports of sintered and annealed films[1].

Table SI1: Details the optimization of solvent ratio on substrate effects and successful printed traces



Haxane:Toluene Ratio	Viscosity	Comments
1.1	0.39	No substrate interactions but some spreading issues
1:2	0.43	No substrate effects and best printed trace appearance
1:3	0.46	Observed effects from toluene interacting with substrate

Table SI2: Details the optimization of ink concentration on the density of the printed traces.

Concentration (mg/mL)	Ink Temp (° C)	Plate Temp (° C)	# Print Passes	Comments
15	30	45	5	Observed sparse packing of particles
20	30	45	5	Little change observed from 15 mg/mL
30	30	45	5	Packing improved but still not compact
45	30	45	5	Observed dense packing of particles

Table SI3: Details the optimization of plate (and subsequent substrate) temperature on both the flexible kapton substrate and solvent evaporation.

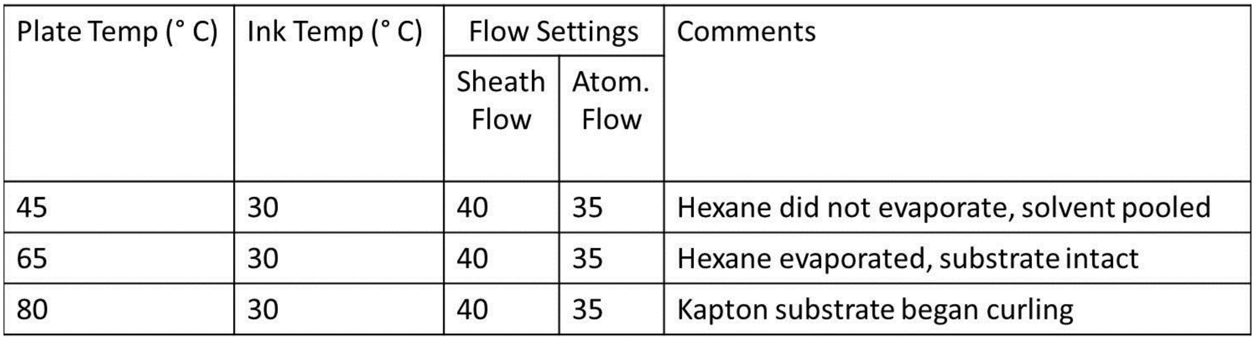
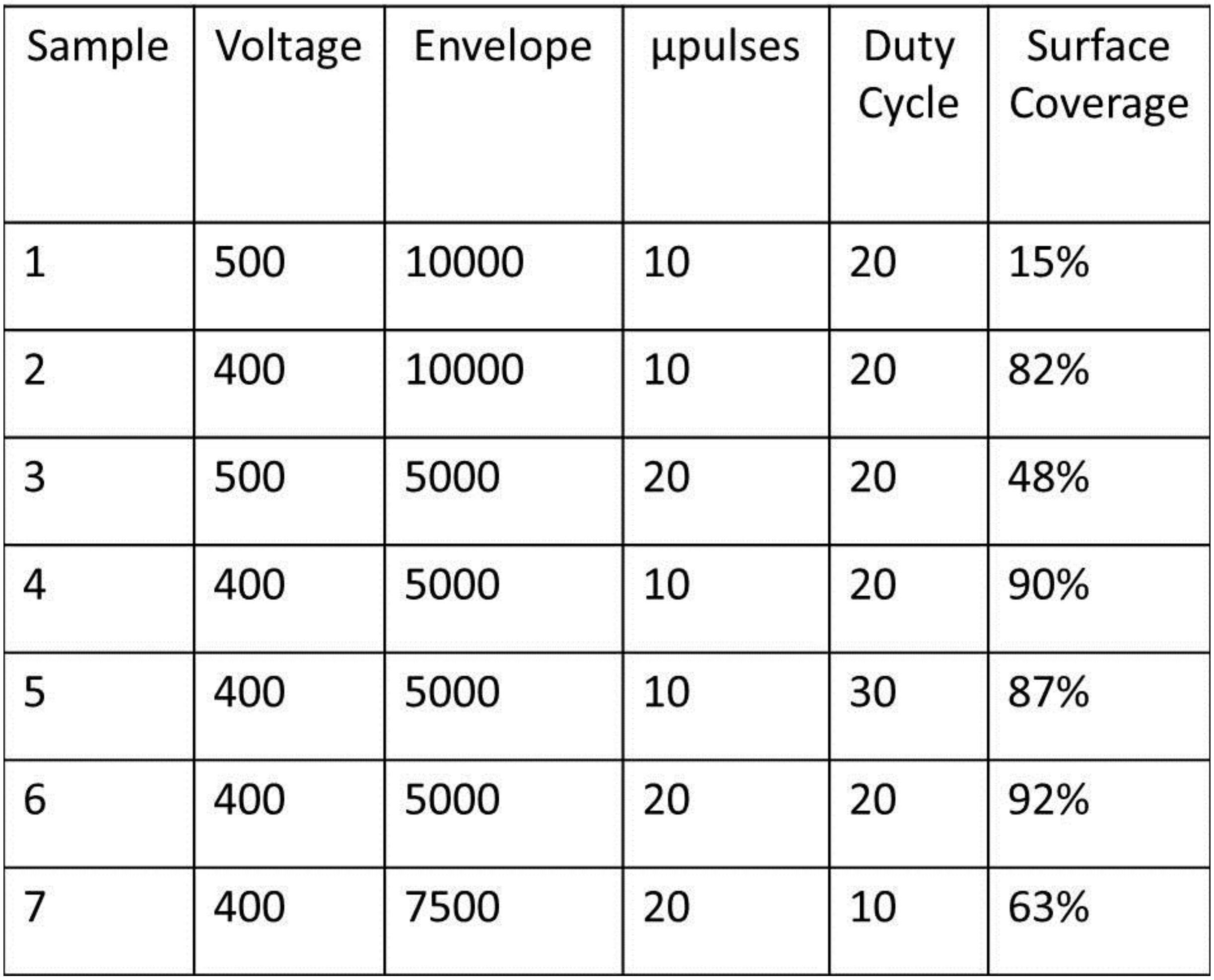


Plate Temp (° C)	Ink Temp (° C)	Flow Settings		Comments
		Sheath Flow	Atom. Flow	
45	30	40	35	Hexane did not evaporate, solvent pooled
65	30	40	35	Hexane evaporated, substrate intact
80	30	40	35	Kapton substrate began curling

Table SI4: Details the optimization of sheath and atomic flow optimization.

Sheath Flow	Atom. Flow	Current	Plate Temp	# Passes	Comments
40	35	400	65	5	
40	38	400	65	5	
45	38	400	65	5	Pressure to high
45	40	400	65	5	
40	42	400	65	5	
45	42	400	65	5	Pressure to high

Table SI5: Details of how the conditions and parameters of the photonic sintering by varying voltage, envelope, µpulses and duty cycle effect film quality and surface coverage.



Sample	Voltage	Envelope	µpulses	Duty Cycle	Surface Coverage
1	500	10000	10	20	15%
2	400	10000	10	20	82%
3	500	5000	20	20	48%
4	400	5000	10	20	90%
5	400	5000	10	30	87%
6	400	5000	20	20	92%
7	400	7500	20	10	63%

1. Peng, P., Hu, A. & Zhou, Y., *Laser sintering of silver nanoparticle thin films: microstructure and optical properties.* Appl. Phys. A, 2012. **108**.