Precious Metal Silver Additive Manufacturing Techniques

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Abstract: Inkjet printing method using conducting silver nano particles for the manufacture of less cost and complex electronic components like sensors, transistors, stretchable heaters etc. The conductivity of the printed pattern plays a crucial role in the performance of the component. To enhance the conductivity of pattern using thermal sintering including heat inert gas technique and induction sintering. The conductivity of the sintered patterns shows better electrical conductivity as almost equal to the bulk silver. Electrohydrodynamic jet printing is a fast production method and its important feature is application of voltage between nozzle and substratum made it suitable microscale electronic devices. Electrohydrodynamic jet printing applications and problems encountered in printing, possible solutions to overcome them.

Introduction:

The numerous advantages of Additive Manufacturing with respect to traditional and subtractive methods plays a vital role in manufacturing sector. The key advantages of AM are design flexibility, ability to produce near shapes and end use parts, lesser time to market the product, reduced supply-chain process and treatments after processing, less wastage with maximum material utilization. A wide range of products are manufactured using AM process, but focus on fabrication of precious metals such as silver, gold, platinum and their alloys are limited. To make customized products with a more precision and accuracy, jewelry industries are focusing on computer driven processes[1].

Metallic nanoparticle inks are mostly used in additive manufacturing as they show better electrical conductivity as compare to other metallic inks. Metallic nanoparticles are normally provided with thermally degradable and nonconductive outer layer and hence they have less conduction. Therefore, postprocessing process technique such as sintering is used to better the electrical conductivity in printed patterns.

Printed electronics is a method for creating electrical components on different substrates using methods such as offset lithography, flexography or inkjet printing. Many factors drive this curiosity are huge production process with minimum price, need of shapeable and throwaway equipment and need for rapid electronic fulfillment. Printed electronic devices are strain sensors, heat sensors, image processing sensors, humidity measuring sensors and bio sensors.[2]

Inkjet printing has number of advantages like low temperature processing, fabricating at low cost and substrate pattern combativeness due to direct writing feature. In addition, micron-sized patterns can be created by DOD without prebuilt masking and etching. In inkjet printing of a conductive nanoparticle pattern, opting of the sintering process is a crucial factor in obtaining stabilized conductivity of the patterns processed as electrical performance mainly depends on the interconnection of individual nanoparticles onto the substrate after buildup by inkjet writing.

Methods:

Sintering:

Sintering is a main process because it determines the electrical conductivity of the pattern produced. The encapsulated organic additives and soothing agent around the metal nanoparticles is decomposed by introducing the energy into the patterns with sintering process and combine the adjacent metal nanoparticles into a single continuous electrical conductivity[3].

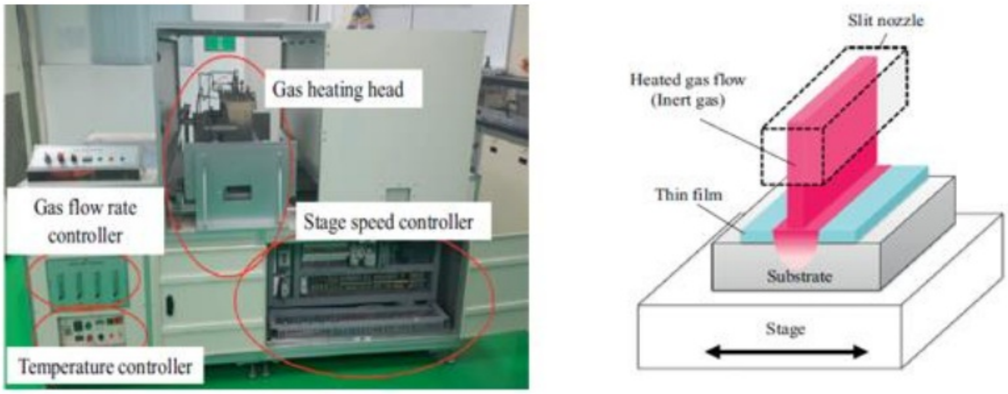
Thermal Sintering:

Thermal sintering for sintering metal nanoparticles inks are in demand because of its low cost, reliability and ease implementation. Thermal sintering is a time-consuming process and needs temperature between 100 °C and 300 °C to sinter metallic nanoparticle inks effectively. Various type of sintering processes available like impulse light, laser sintering etc to overcome the issues like time and temperature in thermal sintering, but they are robust and costly, and they have some disadvantages too. Hence there is a need for research in low temperature sintering process with fast processing speed and to produce high electrical conductivity sintered patterns with minimal flaw to the substrates and patterns[3].

Thermal Sintering using heat inert gas:

Thermal sintering process by using heated gas flow is a modern system for the development of PCBs by characterizing printed silver patterns with reliability. N_2 gas is heated by passing it through a heating head in between temperatures 300 ^{0}C to 700 ^{0}C and it is passed through a nozzle with length around 390mm and 5mm narrow onto the substrates. The sintering characteristics is controlled by the rate of flow of gas, temperature of the heating head and exposure time of gas flowing. The effectiveness of the printed silver pattern by sintering is tested by analyzing of the electrical resistance and metallographic structures with respect to change of temperature at heating head[2].

In this experiment Ag ink with 50nm silver particles of nano size were spread in a tri ethylene glycol monomethyl ether solution. The Printing system consists of print head, motorized stage in XY direction, heat able working table and an alignment system. Before the commencement of the experiment, the droplets expel from the nozzle is governed by managing the voltage and piezo actuator drive waveform before starting printing patterns to print stable single droplet deposition during all the experiments. They used Pi and FR4 as the materials for substrate. The substrates were ultra-sonicated in acetone and 2-propanol alcohol for a span of 10min to eliminate impurity on the surface, rinsed with de-ionized water and then dried in a convection oven at a temperature of 110 ^{0}C.



(a) (b)

Figure 1: Heated N2 gas flow sintering process: (a) Sintering setup; (b) Sintering process[2].

During exposure to the heated N2 gas flow, the surface temperature change is analyzed using colorimeter thermo label sensors before starting of the sintering of Ag patterns.

Electric resistance of the Ag thin films was measured to find the thermal sintering performance of the N_2 gas flow heated sintering system. Electrical resistivity is a main variable in characterizing the sintered Ag patterns after the sintering process as a metal electrode.

Electrical resistivity of Ag film reaches to about 4× 10−8 Ω·m when sintered by heated N_2 gas flow at a temperature of 600^{o} C

After being sintered by the heated N_2 gas flow at 600^{o} C, electrical resistivity of Ag film reaches about 3.96 × 10−8 Ω·m. Calculated electrical resistivity is about 2.5 times of bulk Ag metal (1.6 × 10−8 Ω·m) but 30% lower than the convection oven sintered silver film at 250^{0} C. for 60 min.

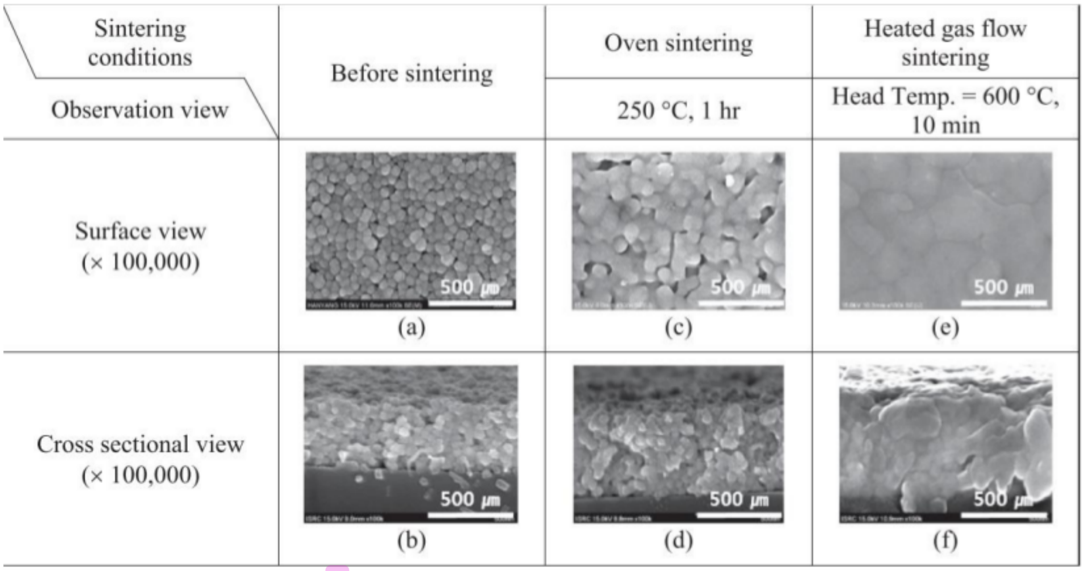


Figure 2: SEM images of Ag film before and after sintering[2].

The SEM images of the Ag film shows the neck growth, growth in grains and pores in the overall intra-microstructure. However, N2 heat gas sintering shows a closely packed microstructure with large grain size of about 300 nm with very less pores in it.

The SEM analytical results show why the Ag film's electrical resistivity sintered by the heated N_2 gas flow shows 30% percent lesser than the Ag film sintered in a convection oven. It is thought that additional contacts between the nanoparticles without porous growth led to reduction of electric resistivity.

Induction sintering:

A robust induction sintering technique is proposed to overcome many issues facing by the present sintering processes. To utilize the mechanism of induction in sintering metallic nanoparticle inks, the printed patterns must be pre sintered to achieve some initial electrical conductivity. Thermal sintering is most reliable as well as time-consuming process for sintering metallic components, but due to its most stability it is used as pre-sintering process before induction sintering[3].

Circular patterns with 10mm diameter were printed on the polyamide substrates with one layer of silver nanoparticles using Optomec Aerosol Jet System at room temperature. To have better electrical conductivity after the sintering process, the thermal pre-sintering temperature should be above the silver nanoparticle ink's organic additives decomposition temperature. Electrical conductivity of the pre-sintered patterns depends mainly on the sintering time and temperatures of the pre-sintering process. To achieve good electrical conductivity for the printed patterns, longer sintering time with low temperature or shorter sintering time at high temperatures are required. The printed patterns were first pre-sintered thermally using convection oven for 60 min at 120 ^{0}C to introduce initial electrical conductivity and to decompose bulk of organic additives present in the printed patterns. Electrical resistivity of the pre-sintered patterns is 1.352 × 10^-7 Ωm.

Simply place the thermally pre-sintered printed patterns over the induction coil and activate the induction heater to induce eddy currents within the printed patterns. It should be noted that, during the induction heating process the printed patterns should be put directly on top near the induction coil for efficient heating where the magnetic field is most steady and concentrated. Induction heating mechanism is non-contact, fast and selective and is commonly used to heat electrically conductive materials directly. It is also extremely advantageous since the induction heating mechanism can separate conductive materials from non-conductive materials to heat, in which alternating electromagnetic field only heats up electrically conductive materials. The alternating electromagnetic field interacts with the conductive workpiece and generates eddy currents inside the work piece. Through the Joule heating effect, the induced current creates a heating effect within the conductive workpiece.

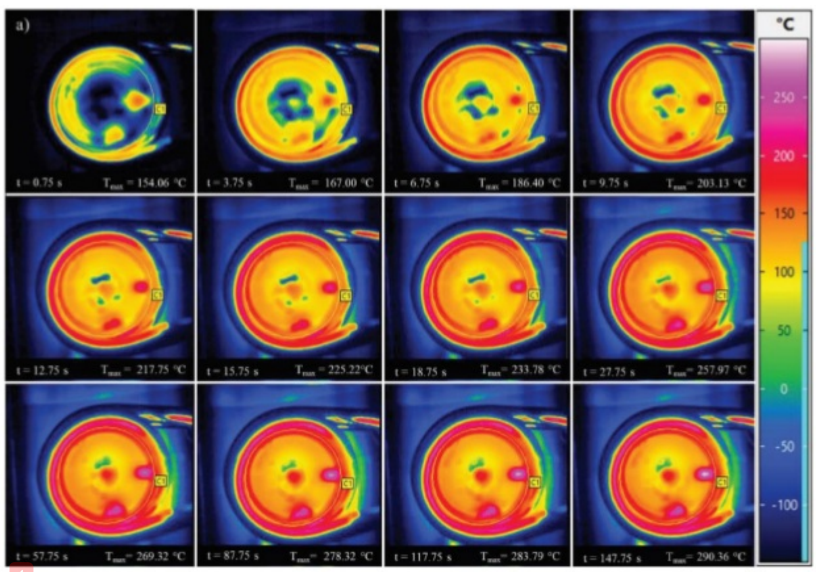


Figure 3:Printed pattern thermograms during induction sintering at different times[3].

Due to higher concentrations of magnetic flux around the circumference of the induction coil, the printed pattern appears to get heated up at the rims first during the induction sintering process. The heat generated at the rims of the printed patterns from the eddy current losses was then carried toward the center of the printed patterns. During the induction sintering process, the entire printed pattern was heated uniformly by thermal conductivity, as silver is an excellent thermal conductor. The induction sintering process approximately took five cycles to uniformly heat the entire heated pattern. The maximum temperature of the printed pattern was maintained under 300 ^{0} C during the induction sintering process to prevent deformation and deterioration of the polyimide substrate. After the induction sintering process, no visible defects and damages were also observed on both printed patterns and substrates.

Table 1:

Sintering Process	Sintering Parameters	Time Taken	Average electrical resistivity (Ω m)	Average conductivity (% of bulk silver conductivity)
Induction-sintering	Pre-sintered for 60 min at 120 ^{0} C	60 min	1.98 × 10^-8	81.07
Thermal sintering	200 ^{0} C 240 min	240 min	3.97 × 10^-8	40.37

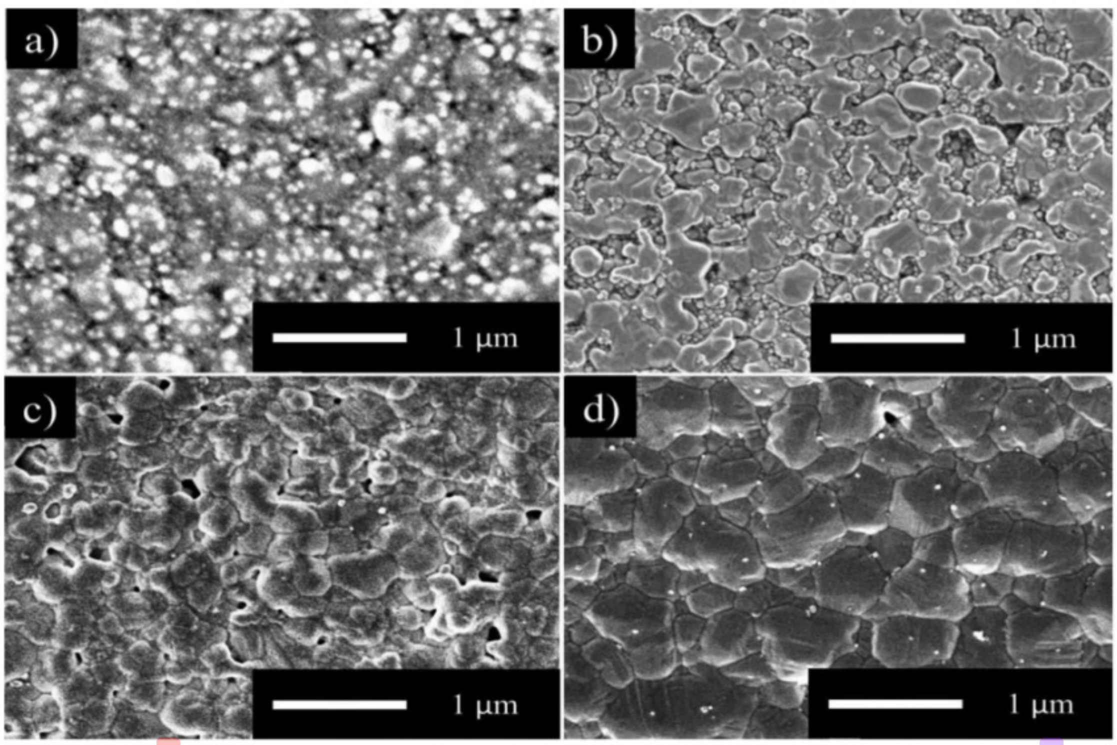


Figure 4: FESEM images of the silver nanoparticle ink printed patterns: a) un-sintered, b) thermally pre-sintered at 120 ^{0} C for 60 min, c) thermally sintered at 200 ^{0} c for 240 min d) induction-sintered[3].

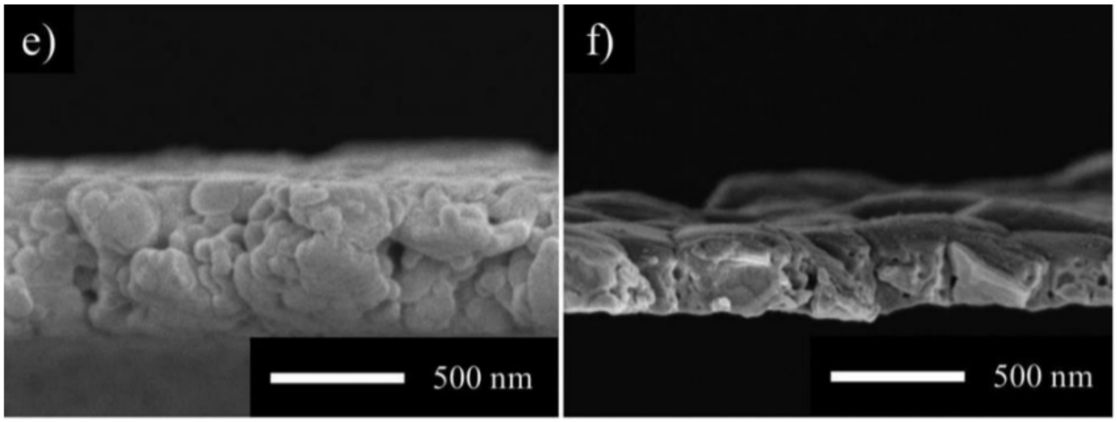


Figure 5: e) cross-sectional view of thermally sintered at 200 0 C for 240 min f) cross-sectional view of induction sintered[3].

Sintering by Induction technique proves to be an innovative and efficient process for silver nano particle ink and it can be extended for sintering other types of electrically conductive metal nano particles inks. The electrical resistivity of the induction-sintered printed pattern was measured shows 81% conductivity of bulk silver.

Compare to thermal sintering, patterns sintered by induction technique proves to have denser microstructures and higher electrical conductivity. Induction sintering proves to be more effective and energy efficient as compared to thermal sintering since it only heats the electrically conductive printed patterns rather than entire substrate.

Electrohydrodynamic Jet Printing:

Electrohydrodynamic jet printing is a fast production method in additive manufacturing fields that can produce many types of micro-nano structures, from metal to polymer. There are many advantages of electrohydrodynamic jet printing such as fast output, low cost, mask free and pattern variation, making it possible to manufacture many practical structures[4] .The nano ink for printing are prepared by nanomaterials and typical solvent, resulting in the good property for printing with silver nanoparticles, silver fibers etc.

Printing parameters such as voltage, shifting speed, frequency, standoff distance, needle size greatly influence the property of the printed results which showed high aspect-ratio 3D structures of sub 10µm resolution by e-jet printing[4].

Potential applications for printed metal structures is radiation shielding. Due to heavy intensity radiation, the electronic components and circuit board used in a high radiation setting often cause device operational errors. Silver micro-structures in dots, lines and other designed patterns were fabricated by e-jet printing. Printed silver structures are good candidates for radiation shielding in circuit boards and electronics.

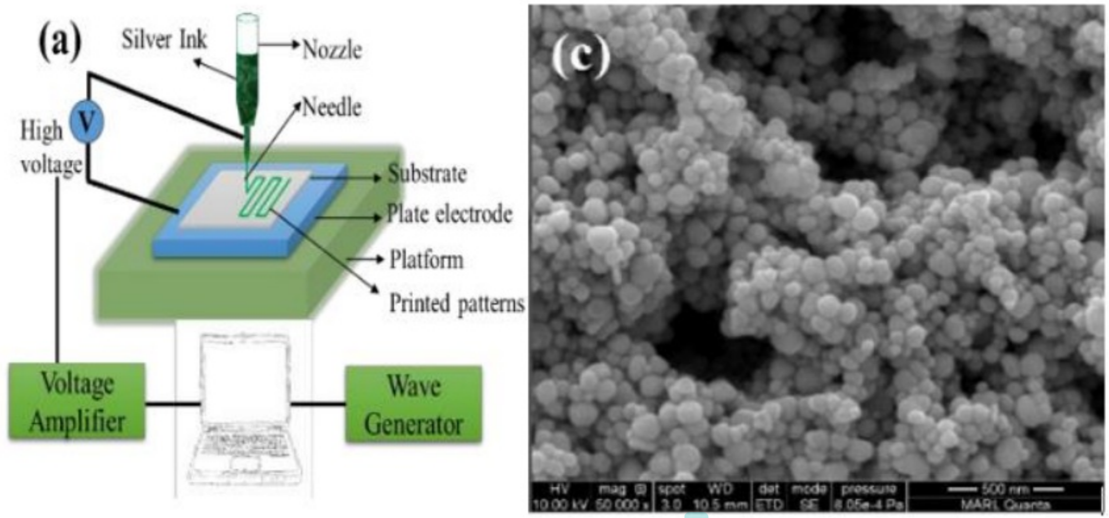


Figure 6: (a) Process of electrohydrodynamic jet printing (c) SEM image of printed silver dots[4].

Voltage is a key parameter of electrohydrodynamic jet printing. High voltage electrical field is used as a force for jetting of nano inks. In Electrohydrodynamic jet printing, the droplet from the nozzle is controlled better using voltage as compared to jet printing driven by gas. Figure 6 (c) consisting of dense silver nanoparticles, indicating that the stability of nano particles is not disturbed in the electrohydrodynamic jet printing process.

Application of Electrohydrodynamic jet printing:

Organic thin film transistors has been intensively investigated due to their excellent advantages in both processing and applications. While graphene grown using chemical vapor deposition (CVD) shows excellent conductivity, transparency and mechanical properties, there is still a need to improve the conductivity levels of ink-type carbon nanomaterials. Alternatively, metal nanowires like silver nanowires (AgNWs) have become promising candidates because of their appealing electrical, thermal and optical properties. The method used to pattern AgNWs is important in improving the electrical and mechanical properties when used in OTFTs.

The important feature of EHD jet printing, which differentiates from other jet printing techniques such as inkjet printing, is application of a voltage between the nozzle and substratum.

EHD inkjet printing is an attractive manufacturing method for microscale electronic devices since this process can obtain fine resolution features and is compatible with a variety of usable inks. An uniform silver micro tracks with a 35mm µm line width was printed and its resistivity was measured to be in range (2–4)×10−8 Ωm which is 2.4 times of the theoretical values of the bulk silver (1.6 × 10−8 Ωm)[5]

Problems encountered in EHD 3D printing and their possible solutions[5]**:**

Existing Problems	Solutions
Increasing precision of placement.	Maintain minimum distance between substrate and nozzle end.
To increase yield rate	Increasing number of nozzles.
Alleviating end effects from neighboring nozzle	Insert a non-conductive or dummy nozzle. Insert metal nozzles into non-conductive material based multi nozzle structure. Maintain enough distance between each nozzle. Change in shape of array of nozzles.
Eliminating distance due to surface irregularity of the substrate such as uneven surface, restriction of standoff distance, non - conductive material	Changing configurations of electrodes such as nozzle ring type. Applying sinusoidal AC voltage and print droplet whose charge alternates between positive and negative charges.
Reducing size of the droplet	Reducing flow rate, increasing voltage, minimizing diameter of nozzle outlet.

3D inkjet printing:

3D inkjet printing, a drop on demand process, can manufacture micro sensors in a facile and low-cost way rapidly. Small batch production of electronics with frequent changes like sensors requires successful fabrication. Because of the high conductivity and thermal stability, suspensions of gold and silver nano particles have been commonly used in conductive inks research[6]. Silver nano particles with a diameter of less than 50nm have a significantly lower sintering temperature, usually 160 – 300^0 C compared to the bulk material's melting temperature 963^0 C. Silver nano particles are suitable to form the micro sensors on Kapton substrates.

An electrically conductive nano silver ink used has 40 wt% Ag, viscosity (8-12 cp), surface tension 25-30 dyne/cm and average particle size of 40-60 nm at 25^0 C[6]. Polyamide films are chosen as substrate and preheated to about 60^0 C before sintering. AUTOCAD 2016 software modeled the patterns of the micro sensors. Micro sensors with different layers is printed and dried in the printer at 60^0 C for 30min.The sensors were then sintered at 100^0 C, 150^0 C, 200^0 C,250^{0}C and compared to one without sintering.

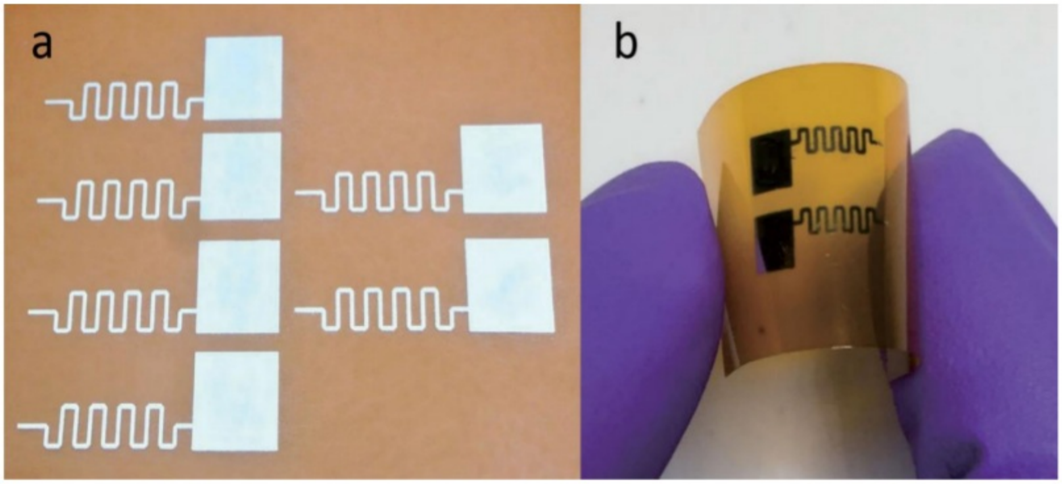


Figure 7: Flexible Micro Sensors[6].

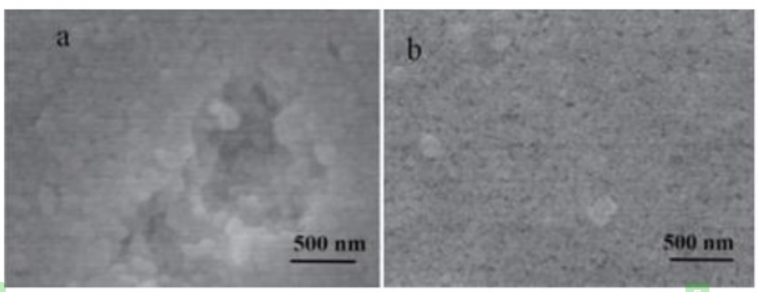


Figure 8(a) SEM image of the silver film before sintering at 200^0 C. (b) After sintering at 200^0 C[6].

The silver nano particles have a clear edge before sintering in Figure 8 (a) and particles were sintered together, and sphere edge disappeared in Figure 8 (b).

Applications:

Electronics:

- Drop on demand (DOD) inkjet printing is widely using in printing graphics and texts for solar cells as it is low temperature method for fabrication, quick and less expensive with quick direct writing[7]. This technique is a twostep process consists of annealing followed by printing. Annealing is opted to fill the voids formed during evaporation of ink due to “coffee ring effect”. Ag line patterns printed on alumina and ceramic glass shows resistivity 30 and 90µΩm which is20 and 60 times greater than silver.
- Inkjet printing technique has become a possible means of producing low cost and sophisticated electronic devices, components and integrated intelligent smart systems like organic thin film transistor, radio frequency identification (RFID) tags, flexible display, stretchable heaters and sensors. Silver has the highest electrical conductivity and high air stability, make it commonly used in electronic devices to produce the conductive patterns. Particle free conductive ink is an alternative to the overcome the challenge, silver conductive ink has been produced which is free of particle, so there is no need to think about the question of nozzle blocking[8].

Conclusion:

Sintering is an important process to enhance the electrical conductivity of the printed patterns. Induction sintering shows 81.07 % of bulk silver conductivity and thermal sintering with 40.37 %. Compare to thermal sintering, printed pattern sintered by induction sintering proves to have denser microstructures and higher electrical conductivity. 3D inkjet printing method mostly suitable for small scale productions whereas EHD is suitable for fast production, low cost, mask free, pattern variation components.

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