



Short Communication

Water vapor-assisted sintering of silver nanoparticle inks for printed electronics



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Abstract

In printed electronics, conductive traces are often produced by printing inks of silver nanoparticles dispersed in solvents. A sintering process is usually needed to make the printed inks conductive by removing the organic dispersants and allowing metal-to-metal contacts among nanoparticles for atomic diffusion and neck formation. It has been challenging to sinter silver nanoparticle inks in a thermal oven at a temperature $< 150\text{ }^{\circ}\text{C}$ to avoid thermal damage to the plastic substrate while achieving desired conductivity. This work presents a simple, yet effective way to sinter a silver nanoparticle ink below $120\text{ }^{\circ}\text{C}$ (even at $80\text{ }^{\circ}\text{C}$) by exposing the printed ink to water vapor in the oven. The results consistently show a significant reduction in line resistivity for the samples sintered in a moist oven compared to those sintered in a dry oven. For example, the measured resistivity can become $9.32\text{ }\mu\Omega\text{ cm}$ (5.90 times that of bulk silver) when a silver nanoparticle ink is sintered with water vapor at $120\text{ }^{\circ}\text{C}$ for 30 min. Hence, solvent vapor-assisted sintering of metal nanoparticle inks can become an enabling approach to broadening the product range of printed electronics.

Keywords Sintering · Metal nanoparticles · Printed electronics · Aerosol Jet[®] printing · Water vapor

1 Introduction

Functional inks consisting of metal nanoparticles dispersed in solvents are commonly used in the printed electronics industry to fabricate conductive patterns on plastic or paper substrates [1]. To prevent agglomeration of those nanoparticles, metal particle-binding thiols and polymers (also called the “capping agent”) are used as dispersants for stabilizing the dispersion [2–4]. Such metal nanoparticle inks can be deposited onto substrates according to designed circuit pattern by a number of printing techniques such as screen printing, syringe-needle type dispenser, inkjet, Aerosol Jet[®], to mention a few. After printing and solvent evaporation, the metal nanoparticle materials usually do not become adequately conductive. The particle–ligand bonds must be broken for the removal of polymeric ligands between contacting particle surfaces to establish metal-to-metal atomic diffusion among particles, because the movement of electrons between metal

particles can be prevented by an organic layer as thin as a few nanometers [5].

As a common practice, sintering the printed metal nanoparticle ink at an elevated temperature (e.g., in a thermal oven) can make it electrically conductive, while the polymeric ligands might be removed by thermal decomposition (known as pyrolysis) and vaporization. Simultaneously, the contacting metal nanoparticles are fused together via interfacial atomic diffusion and neck formation [6]. In some silver nanoparticle ink, the particles appeared to touch each other when heated to $70\text{ }^{\circ}\text{C}$ as the organic molecules started moving away from particle surface; but the electrical resistivity reached minimum value only at a temperature $> 200\text{ }^{\circ}\text{C}$ and then increased with further heating to temperature beyond $250\text{ }^{\circ}\text{C}$ due to growing pore size with reduced connectivity among coalesced large metal domains [7].

Sintering silver nanoparticle inks in a thermal oven, although conceptually straightforward, poses practical

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limitations for printed electronics on common low-cost polymer substrates (e.g., polycarbonate and polyethylene terephthalate) with glass transition temperature well below 200 °C. To avoid thermal damage to the plastic substrate, the printed parts should not be sintered above the heat-deflection temperature of substrate. On the other hand, it is often desired to obtain lowest possible resistivity of the sintered ink material for the desired electronic performance. When producing functional electronic devices, it is also important to have adequate adhesion and cohesion of the sintered nanoparticle material on a substrate, which may also require increased sintering temperature. Thus, development of metal nanoparticle inks for low-temperature sintering has been an ongoing endeavor in the printed electronics industry.

Despite years of intensified research efforts, the ideal metal nanoparticle ink and its sintering process still remain elusive. Besides simply heating the printed parts in a thermal oven, other sintering methods have also been investigated by using localized laser beam [8–11], pulsed light [12], microwave [13], electrical current [14], and so on. Some recent findings have also suggested possibilities for sintering silver nanoparticles even at room temperature when utilizing oppositely charged polyelectrolytes [15], or solvent-absorbing coating on substrate (which also indicated the beneficial effect of humidity) [16], or destabilizing agent activated during solvent removal [17], or potassium chloride solution [18], etc. However, the method of thermal oven sintering is still widely used in printed electronics production for operational simplicity and convenience.

In this work, we present a process of thermal oven sintering by simply placing a measured amount of water in a bottom tray when putting in the samples. The presence of water vapor while sintering has been found to significantly reduce electrical resistivity of a commercially available silver nanoparticle ink (Sicrys™ I60PM-116 by PV Nanocell), when compared to samples sintered without water vapor. When this ink is printed and sintered on polycarbonate substrates, measurements according to ASTM D3359-09 show that all the samples pass 5B adhesion test rating

even after exposure to “salt spray” in a foggy chamber of 35 °C for 48 h per ASTM B117-11.

2 Experimental methods

As is typical with printed electronics, the silver nanoparticle ink is deposited according to the test pattern on a substrate by a printing process, and then sintered in a thermal oven with adjustable process settings for temperature, duration, and amount of water. In the present work, an Aerosol Jet® direct-write system [19] is used for printing and a Cole-Parmer® vacuum oven (StableTemp Model 281A) is used for thermal sintering. The printed samples are sintered in an oven chamber with a tray on the bottom containing a measured amount of water, at a set temperature under ambient pressure without active gas pumping.

The test samples for resistivity evaluation are printed with consistent line length L , width W , and cross-sectional area A_x with probe pads for four-point resistance measurement (as shown in Fig. 1), according to a given mass output from the Aerosol Jet® deposition nozzle. After being sintered, the resistance of each printed line R is measured with the four-point probe method. The value of resistivity, ρ , is then determined according to

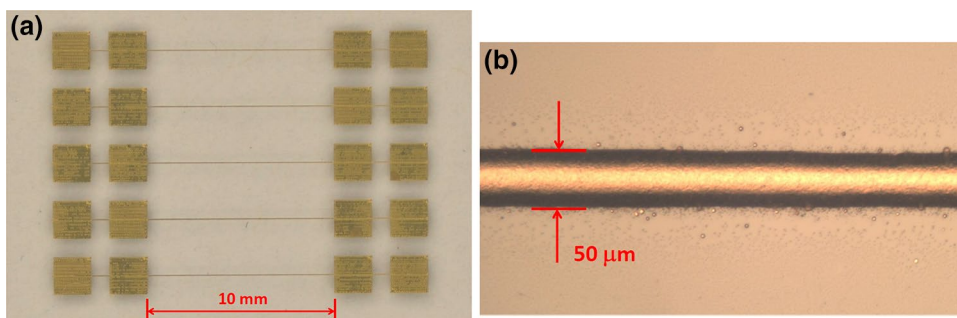
$$\rho = \frac{RA}{L}, \quad (1)$$

where the value of cross-sectional area, A , may be considered simply as that from the measured line profile, A_x , in Fig. 2, which could vary depending upon the sintering condition and packing density of the nanoparticles.

An alternative way for determining A is to use a calculation based on the metal mass deposition rate, μ (which can be maintained at a consistent value during Aerosol Jet® printing) and the bulk metal density, ρ_m , with the known print speed, u , as

$$A_m = \frac{\mu}{u \rho_m}. \quad (2)$$

Fig. 1 **a** Aerosol Jet®-printed 10-mm-long lines on glass with probe pads for four-point resistance measurement and **b** optical microscope image of a line segment. The line width is measured as 50 microns on a micrometer-controlled stage



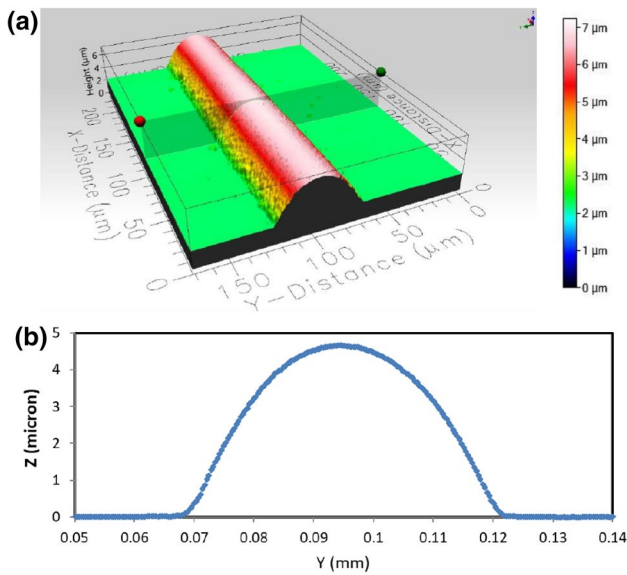


Fig. 2 Optical profilometry results of the Aerosol Jet®-printed line in Fig. 1 using the Filmetrics Profil3D based on white-light interferometry, with **a** being the 3D view and **b** the line profile from extracted data. It is shown that the line is 0.05 mm (or 50 μm) wide with a cross-sectional area of $A_x = 163 \mu\text{m}^2$ when sintered at 200 °C for 60 min with 10 grams of water placed in the oven tray

The value of A_m from (2) actually corresponds to the effective cross-sectional area of the metal material, whereas A_x is the geometric cross-sectional area of the porous material. Thus, using A_m determined by (2) for A in (1) removes the often uncontrollable variable of particle packing density. For the sample shown in Fig. 2, as printed with a metal mass output rate $\mu = 0.75 \text{ mg/min}$ (or 0.0125 mg/s) at a speed of $u = 10 \text{ mm/s}$, using $\rho_m = 10.5 \text{ mg/mm}^3$ for bulk silver yields $A_m = 119 \mu\text{m}^2$ according to (2), whereas the geometric cross-sectional area is measured as $A_x = 163 \mu\text{m}^2$ (which corresponds to a density of 7.7 mg/mm^3 or 73% of bulk silver density for the sintered nanoparticle material).

Table 1 Measured resistivity values (in units of the bulk silver resistivity) under different sintering conditions

T (°C) ^a	30 (min)	60 (min)	120 (min)	Water (gram) ^b
120	–	>720	22.62	0
120	5.90	3.24	3.45	10
200	4.39	4.48	4.81	0
200	2.05	2.13	2.07	10

^a T is the oven set temperature

^bAmount of water placed in the bottom tray in the oven chamber

3 Results and discussion

The effect of having 10 grams of water placed in the bottom tray inside the 18-L oven chamber is shown in Table 1, for oven temperature set at 120 °C and 200 °C. The values of relative resistivity, in units of the bulk silver value ($1.58 \mu\Omega \text{ cm}$), are calculated according to (1) from measured resistance R , line length $L = 10 \text{ mm}$, and the cross-sectional area $A = A_m$ determined by (2). After sintered at 120 °C with water vapor for an hour, the line resistivity becomes even less than that sintered at 200 °C in a dry oven. The relative resistivity values are measured as 2.29 and 5.52 for printed lines sintered at 150 °C for 60 min with and without water vapor, respectively. Even at 80 °C, the relative resistivity can become 9.39 if sintered with water vapor for 4 h. Clearly, the resistivity values of printed lines sintered with water vapor are significantly reduced from that in dry oven, especially at lower sintering temperature.

To illustrate the effect of amount of water placed in the oven chamber, Fig. 3 shows the measured resistivity of printed lines sintered at 120 °C for 1 h as a function of water amount. Interestingly, the result of sintering with this process is rather insensitive to the amount of water placed in the oven tray as long as more than 10 grams of water (in an 18 L oven chamber) is provided. Thus, a robust sintering process can be easily implemented by following a simple rule of > 0.5 grams of water per liter of oven chamber volume.

The water vapor mass, M , in the oven chamber of volume, V , may be estimated in terms of the liquid water mass, M_w , placed in the tray and the maximum water vapor mass (based on Amagat’s law of partial volume) $M_{\text{max}} = PV / (R_v T)$ at pressure, P , and temperature, T (with $R_v = 461 \text{ J K}^{-1} \text{ kg}^{-1}$ denoting the gas constant for water vapor) as

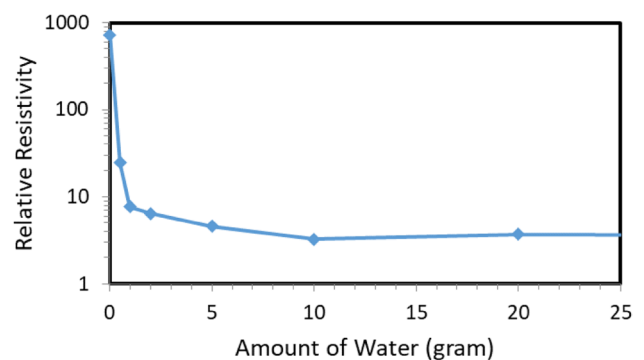


Fig. 3 Measured values of line resistivity (in units of the bulk silver value) as a function of amount of water placed in the oven chamber, for an hour sintering at $T = 120 \text{ °C}$. The flat part for constant resistivity actually extends up to 50 grams of water (as tested), though certain amount of liquid water may remain in the tray at the end of sintering when more than 10 grams of water is used

$$M = M_{\max} \left[1 - \frac{1 - M_i/M_{\max}}{\exp(M_w/M_{\max})} \right], \quad (3)$$

where M_i is the initial water vapor mass inside the oven chamber (which may often be assumed as zero). Here, we have assumed the partial volume of vaporized liquid water to displace the same volume of gas containing a mass density of water vapor M/V , such that P is maintained at a constant value. With $P = 10^5$ Pa, $V = 0.018$ m³ and $T = 393$ K (for 120 °C), we have $M_{\max} \sim 0.01$ kg (or 10 grams of liquid water). If we place $M_w = 10$ grams of water in the tray, the oven chamber would contain $M = 6.3$ grams of water vapor according to (3) for $M_i = 0$. The value of M will approach M_{\max} (= 10 grams) when $M_w/M_{\max} \gg 1$.

The effect of water vapor on the structure of sintered nanoparticles can also be revealed from the scanning electron microscopy (SEM) images in Fig. 4, showing that the presence of water vapor enhances nanoparticle coalescence to form much larger connected (bright) regions of metallic silver. Since the temperature is only 120 °C, thermal decomposition and vaporization of the organic capping agent are not expected to occur, as evidenced by organic materials in the dark regions.

When describing the basic mechanisms for sintering, the metal nanoparticle inks in printed electronics at a temperature (e.g., ~ 150 °C) much lower than the bulk metal melting point T_m (e.g., 960 °C for silver), most researchers would point to the phenomenon of “melting point depression.” However, quantitative results show that significant reduction in melting temperature only occurs for nanoparticles of diameters below 10 nm, while the size of silver nanoparticles in the PV Nanocell ink used here is typically greater than 50 nm with estimated melting point

still above 900 °C [20]. In the powder metallurgy process (with larger particles though), the sintering temperature for a single-component powder is usually higher than $T_m/2$. Then it is difficult to expect sintering of silver nanoparticle inks at $T \sim 150$ °C (as often observed with the silver nanoparticle inks for printed electronics), if based on the mechanism of melting point depression alone.

As their size decreases, nanoparticles will have increased surface-to-volume ratio (which is inversely proportional to the particle diameter). Therefore, there are relatively more atoms on the surface of the nanoparticle. Those surface atoms are generally more energetic, due to weaker intermolecular bonds than those interior ones. Liquefaction of solid surface below T_m (or “surface pre-melting”) had indeed been directly observed [21]. Based on several recent publications [15–18], the phenomenological knowledge seems to suggest that the key for successful sintering of metal nanoparticle inks at low temperature is to facilitate the removal of the organic capping agent from the contacting gap between adjacent particles. Once the metal particle-to-particle contact is established, the intermolecular attraction due to van der Waals forces may be sufficient to bring about effective coalescence of particles. According to a computational model with Lennard-Jones potential, contacting spherical particles under the influence of attractive intermolecular forces would deform to have finite (nonzero) contact area [22, 23]. Across such a contact area, atomic diffusion is expected to happen spontaneously for neck growth between coalescing particles even at room temperature, as revealed by molecular dynamics simulations [24]. Hence, finding the most convenient way to remove the organic capping agent from the particle contacting gap can be an effective approach to enable low-temperature sintering of metal nanoparticle inks.

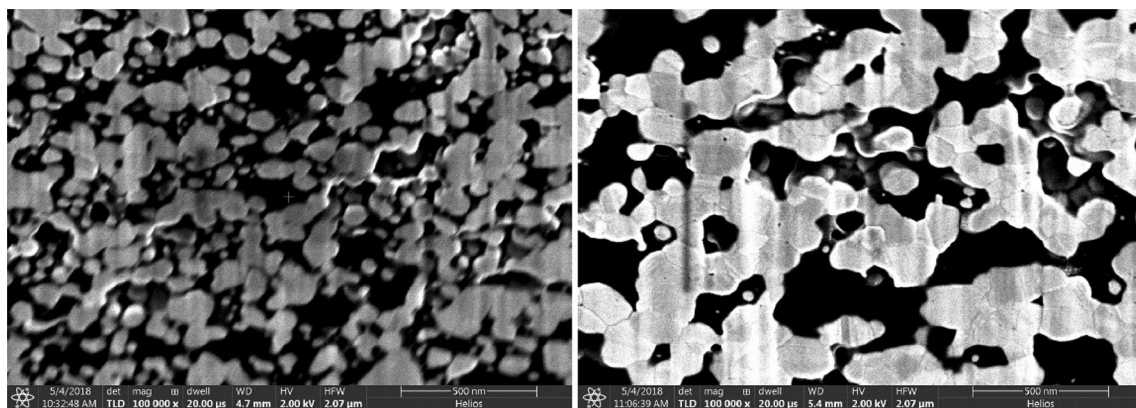


Fig. 4 The SEM images (with the same 500-nm scale bars) of sintered silver nanoparticles at 120 °C for 2 h in a dry oven (left) and that with water vapor (right). The bright regions are the metallic

silver, while the dark regions represent the nonconductive material such as organic capping agent and voids

Generally speaking, the primary outcome of sintering is a reduction in surface area due to atomic motion for neck growth and formation of interparticle bonds. When a liquid phase coexists with a particulate solid at the sintering temperature, the rate of interparticle bonding is usually increased by liquid capillary action which has an equivalent effect of using external pressure as with hot pressing (to densify powder compacts while lowering T_m). In fact, many commercial ceramic products are actually fabricated with a liquid phase present during sintering [25]. Many silver nanoparticle inks use polyvinylpyrrolidone (PVP) as the capping agent. The glass transition temperature of PVP has been known to be lowered significantly when absorbing moisture, possibly to liquefy PVP even below room temperature [26, 27]. Thus, it may be understandable to find enhanced sintering outcomes with certain types of silver nanoparticle inks by introducing water vapor in the oven chamber. With the small pore sizes among nanoparticles, capillary condensation is expected to happen even at low vapor pressure in the diminishing gaps between contacting particles and the capillary attraction due to a wetting liquid to expedite neck growth during sintering process.

4 Concluding remarks

In summary, we have demonstrated an easy and robust method for successfully sintering a silver nanoparticle ink in a thermal oven at temperature below 120 °C (event at 80 °C) by simply placing an adequate amount of water therein. The obtained values of electrical resistivity of sintered ink with water vapor assistance can become about three times the bulk silver resistivity, while maintaining 5B adhesion test rating on polycarbonate substrates even after exposure to “salt spray” by measurements according to ASTM D3359-09. Although results only for the silver nanoparticle ink from PV Nanocell are presented here, we also obtained similar beneficial effects of water vapor-assisted sintering with several other silver nanoparticle inks (e.g., that of Advanced Nano Products, PARU, NovaCentrix, etc.) Using water as the vapor solvent in the present work is mainly for its simplicity in laboratory implementation; other solvents may also be considered depending on particular ink formulations, as yet to be explored. Our results suggest a new research direction for solvent vapor-assisted sintering of metal nanoparticle inks at lower temperatures, to enable broadening the product range of printed electronics.

Although our present work mainly focuses on sintering the silver nanoparticle inks—as widely used for producing conductive patterns in printed electronics, “particle-free” silver complex inks and reactive silver inks have also been developed. For example, a silver complex ink was shown to

become quite conductive after heating at 120 °C for 5 min [28], while “self-catalyzed copper–silver complex inks” were demonstrated to produce “highly oxidation-resistant and conductive copper–silver hybrid tracks” at a temperature below 100 °C [29]. Some printed electrodes with particle-free reactive silver inks may exhibit electrical conductivity equivalent to that of bulk silver upon annealing at 90 °C [30]. Those promising particle-free inks certainly deserve serious attention for further investigation in terms of print quality, throughput, adhesion to substrate, and mechanical robustness.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

References

1. Coatanea E, Kantola V, Kulovesi J, Lahti L, Lin R, Zavodchikova M (2009) Bit bang—rays to the future. In: Neuvo Y, Ylonen S (eds), Helsinki University Print, Helsinki, Finland, pp 63–102. <http://lib.tkk.fi/Reports/2009/isbn9789522480781.pdf>
2. Bonnemann H, Richards RM (2001) Nanoscopic metal particles—synthetic methods and potential applications. *Eur J Inorg Chem* 2001(10):2455–2480
3. Lee KJ, Jun BH, Kim TH, Joung J (2006) Direct synthesis and inkjetting of silver nanocrystals toward printed electronics. *Nanotechnology* 17(9):2424–2428
4. Rajan K, Ropolo I, Chiapone A, Bocchini S, Perrone D, Chiolerio A (2016) Silver nanoparticle ink technology: state of the art. *Nanotechnol Sci Appl* 9:1–13
5. Lovinger AJ (1979) Development of electrical-conduction in silver-filled epoxy adhesives. *J Adhes* 10:1–15
6. Greer JR, Street RA (2007) Thermal cure effects on electrical performance of nanoparticle silver inks. *Acta Mater* 55:6345–6349
7. Chou K-S, Huang K-C, Lee H-H (2005) Fabrication and sintering effect on the morphologies and conductivity of nano-Ag particle films by the spin coating method. *Nanotechnology* 16(6):779–784
8. Chung J, Ko S, Bieri NR, Grigoropoulos CP, Poulikakos D (2004) Conductor microstructures by laser curing of printed gold nanoparticle ink. *Appl Phys Lett* 84(5):801–803
9. Chiolerio A, Maccioni G, Martino P, Cotto M, Pandolfi P, Rivolo P, Ferrero S, Scaltrito L (2011) Inkjet printing and low power laser annealing of silver nanoparticle traces for the realization of low resistivity lines for flexible electronics. *Microelectron Eng* 88(8):2481–2483
10. Ermak O, Zenou M, Toker GB, Ankri J, Shacam-Diamond Y, Kotler Z (2016) Rapid laser sintering of metal nanoparticles inks. *Nanotechnology* 27:385201
11. Renn MJ, Shrandt M, Renn J, Feng JQ (2017) Localized laser sintering of metal nanoparticle inks printed with Aerosol Jet®

- technology for flexible electronics. *J Microelectron Electron Packag* 14:132–139
12. Kim H-S, Dhage SR, Shim D-E, Hahn HT (2009) Intense pulsed light sintering of copper nanoink for printed electronics. *Appl Phys A* 97:791–798
 13. Perelaer J, deGans B-J, Schubert US (2006) Ink-jet printing and microwave sintering of conductive silver tracks. *Adv Mater* 18:2101–2104
 14. Allen ML, Aronniemi M, Mattila T, Alastalo A, Ojanpera K, Suhonen M, Seppa H (2008) Electrical sintering of nanoparticle structures. *Nanotechnology* 19:175201
 15. Magdassi S, Grouchko M, Berezin O, Kamyshny A (2010) Triggering the sintering of silver nanoparticles at room temperature. *ACS Nano* 4(4):1943–1948
 16. Allen ML, Leppaniemi J, Vilkmann M, Alastalo A, Mattila T (2010) Substrate-facilitated nanoparticle sintering and component interconnection procedure. *Nanotechnology* 21:475204
 17. Grouchko M, Kamyshny A, Mihailescu CF, Anghel DF, Magdassi S (2011) Conductive inks with a “built-in” mechanism that enables sintering at room temperature. *ACS Nano* 5(4):3354–3359
 18. Peng P, Li L, Guo W, Hui Z, Fu J, Jin C, Liu Y, Zhu Y (2018) Room-temperature joining of silver nanoparticles using potassium chloride solution for flexible electrode application. *J Phys Chem C* 122(5):2704–2711
 19. <https://www.optomec.com/printed-electronics/aerosol-jet-technology/>. Accessed 3 May 2019
 20. Son Y, Yeo J, Moon H, Lim TW, Hong S, Nam KH, Yoo S, Grigoropoulos CP, Yang DY, Ko SH (2011) Nanoscale electronics: digital fabrication by direct femtosecond laser processing of metal nanoparticles. *Adv Mater* 23(28):3176–3181
 21. Frenken JWM, van der Veen JF (1985) Observation of surface melting. *Phys Rev Lett* 54(2):134–137
 22. Feng JQ (2000) Contact behavior of spherical elastic particles: a computational study of particle adhesion and deformations. *Colloids Surf A* 172:175–198
 23. Feng JQ (2001) Adhesive contact of elastically deformable spheres: a computational study of pull-off force and contact radius. *J Colloid Interface Sci* 238:318–323
 24. Pan H, Ko SH, Grigoropoulos CP (2008) The solid-state neck growth mechanisms in low energy laser sintering of gold nanoparticles—a molecular dynamics simulation study. *J Heat Transf* 130(9):092404
 25. German RM (1985) *Liquid phase sintering*. Springer, New York
 26. Szakonyi G, Zelko R (2012) The effect of water on the solid state characteristics of pharmaceutical excipients: molecular mechanisms, measurement techniques, and quality aspects of final dosage form. *Int J Pharm Investig* 2(1):18–25
 27. Bhattacharya S, Sharma DK, Saurabh S, De S, Sain A, Nandi A, Chowdhury A (2013) Plasticization of poly(vinylpyrrolidone) thin films under ambient humidity: insight from single-molecule tracer diffusion dynamics. *J Phys Chem B* 117:7771–7782
 28. Shabanov N, Chiolerio A, Isaev A, Amirov A, Rabadanov K, Akhmedov A, Asvarov A (2019) A water-soluble ink based on diamine silver(I) carbonate, ammonium formate, and polyols for inkjet printing of conductive patterns. *Eur J Inorg Chem* 2019:178–182
 29. Li W, Li C-F, Lang F, Jiu J, Ueshima M, Wang H, Liu Z-Q, Sugauma K (2018) Self-catalyzed copper-silver complex inks for low-cost fabrication of highly oxidation-resistant and conductive copper-silver hybrid tracks at a low temperature below 100 °C. *Nanoscale* 10:5254–5263
 30. Walker SB, Lewis JA (2012) Reactive silver inks for patterning high-conductivity features at mild temperatures. *J Am Chem Soc* 134(3):1419–1421

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