We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

186,000

200M

Download

154
Countries delivered to

Our authors are among the

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Selective Laser Sintering of Nanoparticles

Sukjoon Hong

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.68872

Abstract

Selective laser sintering of nanoparticles has received much attention recently as it enables rapid fabrication of functional layers including metal conductors and metal-oxide electrodes on heat-sensitive polymer substrate in ambient conditions. Photothermal reactions induced by lasers rapidly increase the local temperature of the target nanoparticle in a highly selective manner, and subsequent sintering steps including melting and coalescence between nanoparticles occur to fabricate interconnected sintered films for various future applications. The mechanism of laser sintering, as well as possible target materials subject to laser sintering, together with experimental schemes developed to improve the process and potential applications, is briefly summarized in this chapter.

Keywords: laser, optics, nanoparticle, metal, metal-oxide, flexible electronics

1. Introduction

In this chapter, we focus on a specific type of sintering that utilizes laser and nanoparticle as its heat source and target material, respectively. Laser and nanoparticle on their own have interesting properties which are advantageous for conventional sintering process. Laser is a tool with a broad range of parameters and enables numerous responses such as remote temperature manipulation and rapid processing speed which cannot be achieved by other mechanical tools. Nanoparticles, having controllable sizes and shapes, find their application in various fields, and melting temperature depression due to their size effect is one of the key properties for sintering as it reduces the temperature required for the sintering process to a great extent. Laser sintering of nanoparticles—combining these two elements—not only possesses both the abovementioned features but also provides additional virtues and allows facile, damage-free fabrication of functional layers on heat-sensitive substrate to bring novel applications in the form of flexible electronics. Selective laser sintering of nanoparticles is



summarized in this chapter with special emphasis on its mechanism, target material, experimental schemes, and potential applications.

2. Mechanism

Sintering of nanoparticles with other heat sources such as furnace or convection oven has been long studied. In a conventional process, nanoparticles in the form of ink are coated on a substrate with wet processing or diverse printing techniques, followed by bulk heating of the substrate at an elevated temperature. Thermal sintering usually involves long sintering time (>30 min) at high temperatures (>200°C) which are often not compatible with numerous heat-sensitive polymer substrates [1]. The main difference of selective laser sintering is that the heat source is substituted with laser. As a laser beam is focused on the designated spot, the optical energy is directly converted into heat through photothermal reaction to control the local temperature with high selectivity and controllability. Laser processing, including selective laser sintering of nanoparticles summarized in this chapter, is expected to show constant processing characteristics as far as the laser beam is properly controlled. Laser processing has certain advantages in terms of reproducibility compared to other processing techniques. Laser is an essentially massless and sterile tool so that the problems from mechanical holders or the processing tool itself can be largely prevented. Laser beam is not subject to wear and tear as well. These properties of laser help avoiding any contamination of the material being processed to increase the reproducibility of the proposed process.

Photothermal reactions by laser can be activated through various elementary excitation including interband and intraband transitions, and the detailed reaction depends on the type of absorbing material as well as the laser parameters [2]. We consider a continuous laser as a simple heat source as far as the characteristic time for the initial processing step is considerably longer than the relaxation time and no phase change occurs during the heating process. For pulsed laser, pulse duration and shape have strong effect on heating characteristics. A single pulse generally brings rapid temperature increase and subsequent cooling. As a result, the temperature swings up and down in case of multiple pulse irradiation, and the average temperature rise is dependent on the repetition rate [3].

Thermal properties of the target nanoparticle are important subjects in sintering, and it is still true for the laser sintering. Prior to the application of laser sintering, thermal properties of nanoparticle are often investigated in separate steps. The melting temperature of nanoparticle changes abruptly in general due to greatly enhanced surface-to-volume ratio at a nanoscale. Previous investigation on the thermal properties of silver nanoparticles is presented in Section 2 as a representative example. The melting point depression of silver nanoparticles at various sizes is calculated from the Gibbs-Thomson equation as shown in **Figure 1(a)** [4]. It is anticipated from the graph that the silver nanoparticle at ~5-nm diameter exhibits significantly lower melting temperature (~150°C) compared to its bulk counterpart at 960°C. A similar trend can be found in other nanoparticles as well [5–7]. Direct observation of the nanoparticle melting is possible through high-temperature tunneling electron microscope

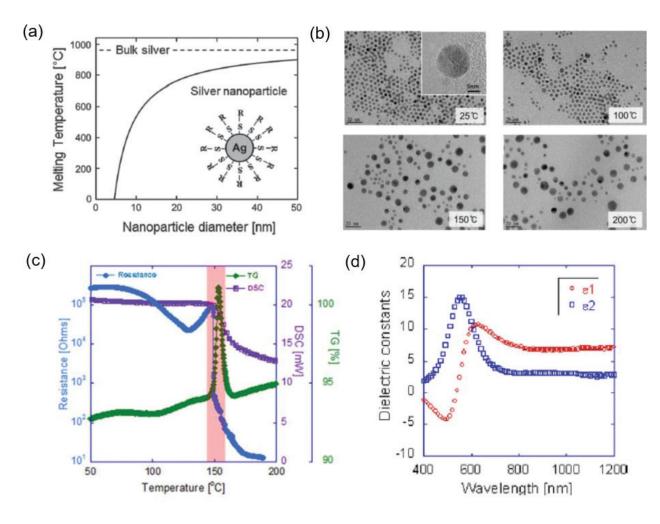


Figure 1. (a) The melting point depression of silver nanoparticles calculated from the Gibbs-Thomson equation. Reprinted with permission from Ref. [4]. Copyrights 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Observation of sintering behavior of silver nanoparticles at various temperatures by in-situ probing. Inset: HRTEM image of a silver nanoparticle with self-assembled monolayer (SAM). Reprinted with permission from Ref. [8]. Copyrights 2012 Elsevier Inc. (c) Melting characteristics of the silver nanoparticles in terms of resistance change (blue), TGA (green), and DSC (purple). Reprinted with permission from Ref. [9]. (d) Ellipsometric measurement of the silver nanoparticle film. Reprinted with permission from Ref. [11]. Copyrights 2008 American Institute of Physics.

(TEM) measurement as in **Figure 1(b)** [8]. The silver nanoparticles show dramatic increase in size when heated at 150°C, while there is no significant change up to 100°C, indicating that the significant melting and coalescence between nanoparticles occur at a temperature as low as 150°C. A more quantitative approach can be found from thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), and electrical resistance measurement according to the temperature as shown in **Figure 1(c)** [9]. A sharp exothermic peak in DSC and a decrease in TGA at ~150°C indicate that there exists a phase change together with the decomposition of the capping organic molecules at the corresponding temperature. The electrical resistance drops rapidly at the same point as the individual nanoparticles melt and merge to provide a continuous conducting path.

Apart from the thermal properties of the target nanoparticles, the optical properties of the material are critical for laser sintering, since photothermal heating characteristics are directly

related to the optical absorption of the nanoparticles. Particles at nanoscale, noble metallic nanoparticles in particular, exhibit unique and tunable optical properties due to their surface plasmonic resonance, and it has been extensively studied for numerous applications. By tuning the nanoparticle size and morphology, together with strong absorption at Rayleigh scattering regime, efficient and local energy deposition can be achieved by a laser. Since laser sintering is commonly applied to nanoparticle film, optical properties of a nanoparticle film are often more practically meaningful in the laser sintering process. Pan et al. [10] extracted the optical properties of silver nanoparticles from spectroscopic ellipsometry and determined its refractive index (n, k) and thickness from direct fitting of measured data. It was shown that a single Lorentz oscillator well explains the dielectric function of the as-deposited film, while two oscillators are required for the sintered films. Such tunability in the optical property is a huge benefit in laser processing as it allows strong absorption at a specific wavelength (Figure 1(d)) to minimize possible damage at other non-processed regions [11].

Sintering is often a many-body problem, yet sintering between two individual nanoparticles has been also investigated through both molecular dynamics simulation and experiments. Necking between two gold nanoparticles can occur even at room temperature (300 K) by local potential gradient, and it is insensitive to laser irradiation as the initial growth occurs very fast (<150 ps) [12]. Molecular simulation shows that major neck growth mechanisms during laser sintering can vary according to the particle sizes, which might include grain-boundary sliding/dislocations, surface diffusion, and viscous flow [12]. Laser-induced nanowelding between two metallic nanoparticles has been experimentally confirmed with TEM. Kim et al. [13] reported that gold nanospheres at 13-nm diameter were successfully welded with picosecond laser pulses with 30-ps duration. TEM grids loaded with gold nanoparticles were directly irradiated with the laser, and its high-resolution TEM (HRTEM) image approved that the joint nanoparticles had single-phase nanocontact to have ohmic electrical connection. The time scale required for the absorbed photon energy to be converted into heat is known to be in the picosecond regime [14], however, the nanoparticle coalescence time and dynamics were not well explained earlier. Pan et al. [15] studied laser-induced coalescence of gold nanoparticles supported on a quartz substrate for the investigation of the coalescence time. The gold nanoparticles were fabricated using e-beam lithography for a more systematic study, and pump-and-probe technique has been utilized with 527-nm pulsed laser and 633-nm continuous laser as the processing laser and probing laser, respectively. Timeresolved transmission traces suggested that the coalescence time for melted nanoparticles is at nanosecond scale as shown in Figure 2(a), and this value is reasonably in agreement to the molecular simulation result.

Practically, single laser sintering involves a large number of nanoparticles, and the overall process should be examined in a more macroscopic perspective. Paeng et al. [16] suggested that silver nanoparticle film under continuous wave-laser irradiation goes through certain steps of initial contact, neck growth, and coalescence for complete sintering, and the macroscopic coalescence time measured from pump-and-probe technique is around 10 ms. This value is in accordance with the time lag between laser irradiation and conductive metal electrode formation that was measured by transient resistance change during the laser irradiation

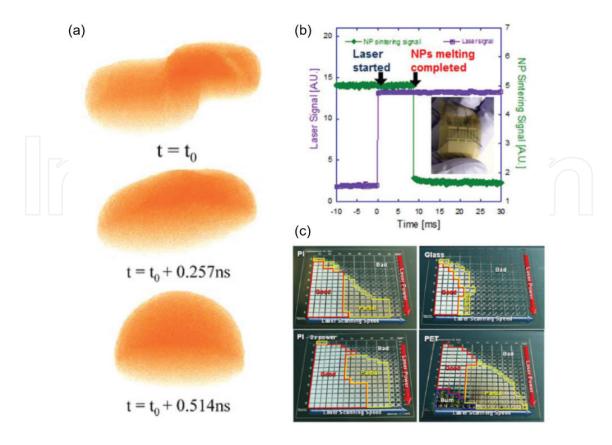


Figure 2. (a) Snapshots of the dynamic coalescence process between two gold nanoparticles from molecular dynamic simulation. Reprinted with permission from Ref. [15]. Copyrights 2008 American Institute of Physics. (b) Transient resistance change measurement according to the laser irradiation. (c) Parametric study for optimum laser conditions on various substrates. Reprinted with permission from Ref. [9].

on silver nanoparticle ink as shown in Figure 2(b) [9]. Since overall laser sintering process is a complex multi-physics problem, which incorporates a number of unexpected issues such as balling defects [17], a parametric study over laser power and scanning speed is often conducted to find the optimum sintering condition experimentally [9]. A typical example of the parametric study is shown in Figure 2(c) with silver nanoparticle film on various substrates. Ag nanoparticle ink was coated on three different substrates—polyimide (PI), polyethylene terephthalate (PET), and glass-and a parametric study in terms of laser power and laser scanning speed was conducted. It is apparent that the status of sintered Ag nanoparticle can be distinguished into three categories, and the area subject to higher laser power and lower scanning speed shows more complete sintering features. Note that there exists damage threshold for plastic substrates such as PI and PET. Due to the monochromaticity of lasers, wavelength is not an easily adjustable parameter in many cases, but the effect of laser wavelength in the sintering process has also been investigated for silver nanoparticles by utilizing three different (diode) lasers [18]. Paeng et al. utilized three laser diodes at 405, 514.5, and 817 nm, whose optical penetration depths are 28.3, 43.5, and 171 nm, respectively, for the Ag nanoparticle film. It was found that surface melting morphologies were observed for the laser wavelength with short optical penetration depth due to the strong surface absorption. The threshold laser powers for sintering were different according to the laser wavelength as well.

3. Materials

In the early stage, metal nanoparticles, the noble metals in particular, were the main target materials for laser sintering due to their low electrical resistance and superior chemical stability. Gold [19–27] and silver [4, 8, 9, 28–35] are the most widely studied materials for laser sintering as conductors at microscale. These nanoparticles are usually prepared in the solution form with a specific solvent at high weight percentage, while small amounts of surfactants are added to prevent unwanted agglomeration or enhance the dispersion of nanoparticles within the solution. For the efficient use of laser, Bieri et al. [19] controlled the diameter of gold nanoparticles so that the absorption depth is minimized at the laser wavelength as confirmed from effective medium theory, Rayleigh scattering, and Mie scattering. Once a focus laser scans the gold nanoparticle film for selective sintering, the remaining nanoparticle solution is washed away with the same solvent used for the nanoparticle ink. It is frequently reported that the topography of the resultant conductor changes significantly with laser parameters [21, 22]. The most obvious trend is that the linewidth widens as the laser power becomes larger, since the area subject to higher intensity than the threshold value for the initiation of the sintering process increases. The morphology of laser-sintered gold nanoparticle line measured by atomic force microscopy (AFM) often shows a bowl-shaped geometry which can be attributed to thermocapillary effects that arise from the Gaussian profile of a focused laser beam. This trend can be also found from the sintering of other metal nanoparticles as well [29]. At high incident laser power, the cross-section morphology of the sintered gold line becomes "sombrero"-like with the rough surface topography [21], and the possible reason behind such a phenomenon might be the substrate deformation as the maximum temperature at the center region exceeds the softening temperature of the underlying substrate. These morphologies are shown in Figure 3(a). Besides examining the resultant morphology of the sintered metal line, macroscopic electrical conductivity is an important factor to evaluate the performance of the laser as a sintering tool. The resultant electrical conductivity is dependent on a number of factors such as particle size, irradiated laser power, and translation speed [24], but it can be as low as only two times higher (5.41 $\mu\Omega$ cm) than the bulk value (2.65 $\mu\Omega$ cm) as in Figure 3(b). The difference could be explained by boundary scattering from polycrystalline structures and trapped residual capping agent inside the sintered conductor. The laser power density for the strong coalescence of gold nanoparticles was measured to be in the range of 9000–14,000 W/cm² [21].

Silver nanoparticle is a good substitute for gold nanoparticles as it shows comparable electrical conductivity with high chemical stability at relatively economical price. The resultant minimum resistivity of laser-sintered silver nanoparticle was as low as 1.59 $\mu\Omega$ cm [9], which is only 130% of the resistivity of its bulk counterpart. One of huge benefits of laser sintering is that the entire process is conducted in ambient conditions at low temperatures which allows using heat-sensitive, cheap polymer as a substrate. A combinatorial study has been thoroughly done for silver nanoparticle to find the optimum laser condition for various substrates including widely used polymer substrates such as Polyethylene terephthalate (PET) and Polyimide (PI) film. **Figure 3(c)** shows that the resistivity of the silver nanoparticle film on the PET substrate initially drops and increases dramatically according to the increase in applied laser

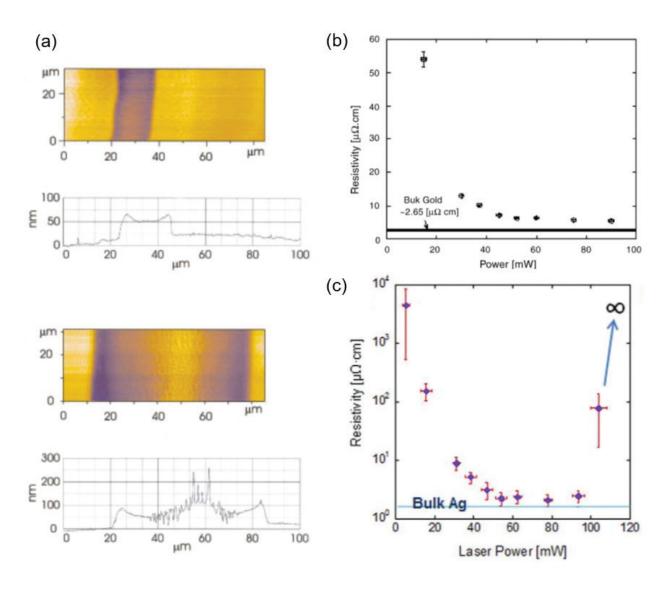


Figure 3. (a) Near-field scanning optical microscopy (NSOM) and atomic force microscopy (AFM) of the sintered gold nanoparticle at (upper) 50-mW and (lower) 300-mW laser power. Reprinted with permission from Ref. [19]. Copyrights 2003 American Institute of Physics. (b) Resistivity of sintered gold nanoparticle electrode at different laser powers. Reprinted with permission from Ref. [24]. Copyrights 2007 Elsevier Inc. (c) Resistivity of sintered silver nanoparticle electrode at different laser powers. Reprinted with permission from Ref. [9].

power due to the thermal damage on the substrate. Minute control of laser power is therefore required for the laser sintering of the metal nanoparticle on flexible substrates. The effect of the underlying substrate has been also confirmed from simulation as well [8]. The mechanical durability of the laser-annealed silver nanoparticle film on the flexible substrate was further tested with outer/inner bending, stretching, cyclic fatigue, and adhesion tests [32]. The laser-sintered silver nanoparticle film shows sufficient mechanical durability, however, void and porosity within the film should be minimized to improve the overall stability.

Recently, more interest has been focused on the laser sintering of copper nanoparticles [36–38] for the replacement of expensive noble nanoparticles. A huge drawback of copper for the sintering process has been its oxidation at an elevated temperature in the ambient condition. Conventional bulk sintering of Cu nanoparticle in ambient condition is often not effective

for its application as a conductive layer. Inert gas environment prevents such a problem of Cu nanoparticles during the sintering at high temperature by blocking the oxygen supply required for the oxidation. However, the use of inert gas unavoidably increases the overall production cost as well as the complexity of the manufacturing. Laser sintering provided a possible solution to this problem by reducing the local sintering time. Zenou et al. [36] investigated the resistivity of sintered copper nanoparticle line at different laser power and scan velocities as shown in Figure 4(a). The minimum resistivity value of the laser-sintered copper lines was found to be highly dependent on the sintering time duration, and the lowest resistivity value was achieved at the shortest local sintering time. At high laser scan velocities, the sintered line resistivity almost approached the resistivity obtained under argon atmosphere, indicating that the oxidation problem is effectively prevented even in ambient conditions by reducing the local sintering time. Kwon et al. [37] characterized the effect of laser sintering of the copper nanoparticle in more detail based on diverse analytic tools including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) and presented that the laser sintering process offers an enhanced chemical stability together with superior oxide suppression in ambient condition.

The application of laser sintering is not limited to metal nanoparticles, and the other class of target nanoparticles include metal-oxide nanoparticles for their conversion into various functional layers. Metal-oxide often requires different laser conditions; for instance, Pan et al. [39]

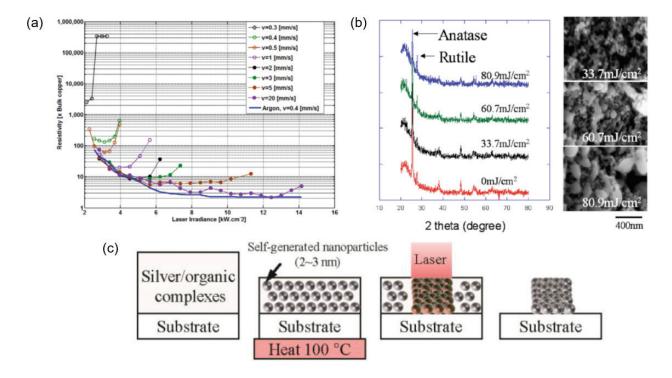


Figure 4. (a) Sintered copper nanoparticle resistivity versus laser irradiance for different laser scan velocities. Reprinted with permission from Ref. [36]. Copyrights 2014 IOP Publishing Ltd. (b) XRD pattern and SEM pictures of TiO2 films on glass after laser annealing with different levels of fluences. Reprinted with permission from Ref. [39]. Copyrights 2012 American Institute of Physics. (c) Process schematics for laser sintering of self-generated nanoparticles from organometallic ink. Reprinted with permission from Ref. [45]. Copyrights 2010 Optical Society of America.

sintered TiO₂ nanoparticles with KrF excimer laser beam at 248-nm wavelength. Laser irradiation not only induced melting and coalescence of these nanoparticles but also phase change from the anatase to rutile for different photocatalytic activity (Figure 4(b)). ZnO nanoparticles were also sintered with the same optical configuration, and it was shown that they transform into interconnected porous structures with a single laser pulse of 160 mJ/cm² to provide enhanced electrical mobility. For the laser sintering of ZnO [40, 41] or TiO [42] nanoparticles, it was found that the environmental gas largely affects the properties of the resultant sintered film since the surrounding gas changes the amount of oxygen vacancy in the sintered nanoparticle film.

Most of the laser sintering process is solely based on photothermal reactions, but reductive sintering incorporates change in the chemical composition of the material upon the sintering process. Representative examples include reductive sintering of CuO [43] and NiO [44] nanoparticles into copper and nickel films. In the reductive sintering, one of the constituent components such as solvent or capping molecules acts as a reducing agent and converts the metal-oxide nanoparticle into metal. Besides the as-prepared nanoparticles, self-generated nanoparticles from organometallic ink [45], or particle-free reactive ion ink [46] is also subject to the laser sintering process as well, following the procedures as in Figure 4(c).

4. Experimental schemes

Being a direct writing and non-contact method, laser sintering contains a number of strengths including high spatial selectivity and mild environmental requirements, yet various experimental schemes have been developed to solve the remaining weaknesses of the laser sintering process such as inefficient use of material, limited resolution, and throughput. Laser sintering of the nanoparticle is a relatively simple process and typically conducted in three different steps: nanoparticle deposition on the substrate, laser scanning, and removal of the remaining nanoparticle as schematically shown in Figure 5(a). Wet coating process such as spin coating or blade coating is the most direct method to prepare the nanoparticle thin film [9, 29], but a large portion of the nanoparticle is wasted as the remaining nanoparticles are washed away after selective laser sintering process. Various approaches to reuse the nanomaterial are under investigation, and the efforts have been also made in terms of experimental schemes to save the amount of deposited nanoparticles in the first place. Chung et al. [21] integrated a dropon-demand jetting system in tandem with continuous Gaussian laser irradiation to conduct nanoparticle deposition and sintering in a single platform. As far as jet printing is concerned, background heating was an important factor to evaporate the solvent during or after printing. Followed by jet printing, focused laser was irradiated to the printed line to further melt and coalesce the nanoparticles selectively. Laser sintering of the jet-printed nanoparticle provided both high uniformity and resolution while saving a large portion of wasted nanoparticles. In a similar way, micropipette was also used to write gold nanoparticle ink prior to the laser sintering [20]. Meanwhile, deposition of thin nanoparticle ink is not easily applicable to certain types of substrates such as polydimethylsiloxane (PDMS) substrate. Lee et al. [28] modified the original process and proposed capillary-assisted laser direct writing (CALDW)

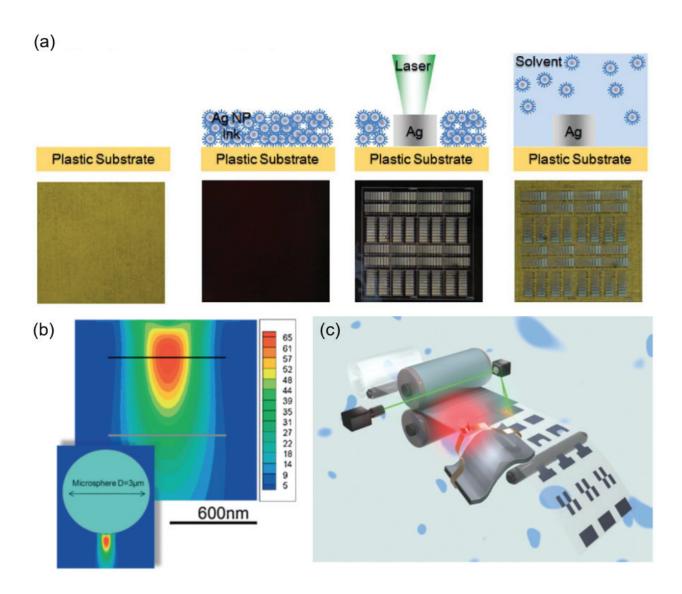


Figure 5. (a) Schematics for typical laser sintering of the nanoparticle. Reprinted with permission from Ref. [9]. (b) Near-field intensity enhancement below the microsphere. Reprinted with permission from Ref. [27]. Copyrights 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) A schematic illustration of R2R system integrated with selective laser sintering technique. Reprinted with permission from Ref. [34]. Copyrights 2015 The Royal Society of Chemistry.

of silver nanoparticle for such a substrate that conducts laser sintering of silver nanoparticle in the colloidal environment. On the other hand, some applications require the thickness of the nanoparticle layer to be several microns, which is difficult to anneal with single laser irradiation due to limited optical penetration depth. For the preparation of such a thick nanoparticle film, Pan et al. [39] combined collision nebulizer with laser sintering to achieve simultaneous deposition and sintering in a single configuration.

Compared to other printing techniques, the minimum feature size achievable by laser sintering process is very small—reaching 2-µm feature size by tight focusing [9]—but often not as good as state-of-the-art photolithography process. Sintering is a thermally activated process in principle, and the resultant temperature distribution is largely determined by the area subject to the photothermal heat generation as well as the heat diffusion from the

heating spot. The amount of heat generation is proportional to the laser intensity in general, and the spatial distribution of the laser intensity at its focus is determined by two factors in principle—wavelength of the laser and the numerical aperture of the lens used for the focusing, assuming that the optical system is reached at its diffraction limit. In order to push the resolution of laser sintering to nanoscale, ultrashort pulse laser or near-field optics has been employed. Son et al. [4] utilized an ultrashort pulsed laser with pulse duration of less than 100 fs, together with a 100 × oil immersion objective lens, to minimize the focused laser's spot size as well as the thermal diffusion from the heating spot. As a result, the uniform sintered line at 380 nm was fabricated with 780-nm wavelength laser. On the other hand, Pan et al. [27] shrank the focused spot size by using near-field optics. Fluidically assembled microspheres at 3-µm diameter were employed as microlens array as shown in Figure 5(b), and the normalized intensity distribution underneath the microsphere calculated by discrete dipole approximation (DDA) confirming that the full width at half maximum (FWHM) of laser intensity at the designated position can be reduced down to 370 nm. The size of sintered dot diameter was as small as 200 nm, which was further reduced to 50 nm in diameter by the simple post annealing process owing to the densification and beading.

Besides, conventional laser sintering process inevitably suffers from low throughput compared to other mass production techniques due to its direct writing nature, and diverse experimental schemes have been proposed to solve this problem. Instead of moving the sample stage, Yeo et al. [9] scanned the laser beam using 2D galvanometric scanning mirror system to increase the sintering speed to a large extent, up to several meters per second. The laser scanner system was controlled by the CAD software to draw arbitrary 2D images, and it successfully fabricated metal micropatterns on a large polymer substrate over a 4-inch wafer in a fraction of minutes. Pan et al. [42] increased the sintering area per single scanning by using a cylindrical lens that produces the focused spot of elliptical cross-section. A large area sintering was feasible with a relatively small amount of scanning by overlapping the extended focus. On the other hand, An et al. [31] introduced digital micromirror device (DMD) as an optical stamp so that an arbitrary 2D pattern can be sintered at a single exposure without any raster scanning, which is often time consuming. 10 × 10 star-shaped silver electrodes with fine-edge sharpness were fabricated by a step-and-repeat scheme to ensure the potential of this process for the large-area metallic micropattern fabrication. The throughput of laser processing can be further increased as the laser system is compatible to other mass production processes. As a proof of the concept, Yeo et al. [33] integrated the laser sintering scheme with roll-to-roll (R2R) printing system to replace the conventional furnace annealing process and boost the area subject to the laser process. The conceptual image of laser sintering process integrated with the R2R system is illustrated in Figure 5(c).

5. Applications

In the early stage, conducting microlines fabricated by laser sintering of metallic nanoparticles was a good alternative for photolithographically defined metal patterns, especially

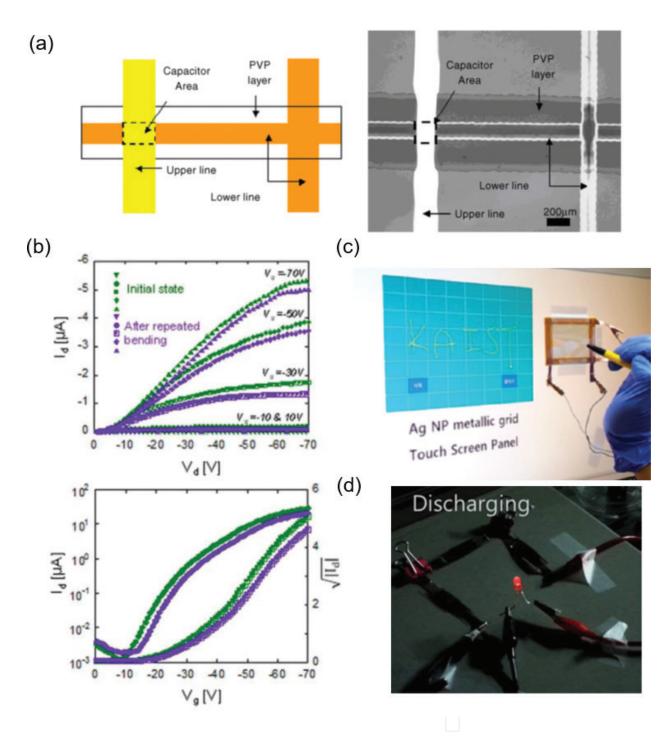


Figure 6. (a) Crossover capacitor schematics on the PI film. Reprinted with permission from Ref. [24]. Copyrights 2007 Elsevier Inc. (b) Output (top graph) and transfer (bottom graph) characteristics of OFET array before and after the bending cycle. Reprinted with permission from Ref. [9]. (c) Demonstration of a metallic grid transparent conductor-based touch panel fabricated by selective laser sintering process. Reprinted with permission from Ref. [29]. Copyrights 2013 American Chemical Society. (d) Demonstration of a series-connected supercapacitor based on laser-sintered nanoparticle current collector to power LED. Reprinted with permission from Ref. [34]. Copyrights 2015 The Royal Society of Chemistry.

for flexible electronics which is not often compatible to the conventional fabrication processes. Laser-sintered microlines were applied to both passive and active electronics, and Ko et al. [24–26] fabricated various electronic components on rigid substrates as well

as polymer substrates by applying successive laser sintering for multilayer configuration. The simplest passive electronic component that requires multilayer structure is a crossover capacitor. For its fabrication, a lower level conductor line was firstly ink-jet printed and processed with laser on a PI film, followed by printing of dielectric layer, and another micro-conductor line as shown in Figure 6(a). The measured capacitance for ~200-nm dielectric layer thickness was 1-10 pF for non-shorted capacitors [24]. A transistor is a representative example of active electronic components, and it has been proven that the conductor microlines fabricated by laser sintering of metallic nanoparticles can well replace the electrodes including gate, source, and drain. For the fabrication of the organic field effect transistor (OFET), carboxylated polythiophene with increased air stability was used as the semiconducting polymer. The carrier mobility of the resultant OFET on silicon wafer with laser-sintered source and drain was measured to be around 0.01 cm²/V, and this value is comparable to the lithographically processed OFET fabricated with the same semiconducting polymer [26]. By expanding the idea and incorporating large-area scanning method, 11,520 OFET arrays were fabricated on a flexible PI substrate with two successive laser sintering processes for source, drain, and gate electrodes [9]. The transistor performance characteristics were measured before and after the 100,000-times bending cycles and confirmed no significant changes in the OFET performance as shown in Figure 6(b). This result validates that the electrical performance of the devices fabricated by the current process is acceptable for broad applications in flexible electronics. On the other hand, Lee et al. [41] utilized laser-sintered ZnO nanoparticle to replace the active channel layer.

Starting from the simple microconductor lines in minute electronic components, potential applications of laser-sintered nanoparticles have been extended to a large extent. Hong et al. [29], Suh et al. [38], and Lee et al. [44] applied laser sintering of silver, copper, and nickel nanoparticles, respectively, to fabricate a large-area flexible transparent conductor based on a metal microgrid structure and utilized it for other optoelectronic devices such as a touch screen panel (**Figure 6(c)**) As the area subject to the laser sintering has increased, laser-sintered nanoparticles find its application in energy devices as well. R2R-printed silver nanoparticles followed by rapid laser annealing is proven to be an efficient way of preparing the current collector for various energy devices including supercapacitors [33, 34] as in Figure 6(d), while sintering of the metal-oxide nanoparticle can be employed for the active electrode layer of solar cells [39]. Besides, the usage of laser-sintered nanoparticles is still under investigation as in the example of the nanocomposite of a nanowire-reinforced nanoparticle matrix film [35].

Acknowledgements

This work was supported by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy. (No. KETEP20174010201310)

Author details

Sukjoon Hong

Address all correspondence to: sukjoonhong@hangyang.ac.kr

Department of Mechanical Engineering, Hanyang University, Ansan, Gyeonggi-do, Republic of Korea

References

- [1] Cummins G, Desmulliez MPY. Inkjet printing of conductive materials: A review. Circuit World. 2012;38(4):193-213
- [2] Bäuerle DW. Laser Processing and Chemistry. Springer-Verlag Berlin Heidelberg; 2013. pp. 3-62
- [3] Eaton SM, Zhang H, Herman PR, Yoshino F, Shah L, Bovatsek J, Arai AY. Heat accumulation effects in femtosecond laser-written waveguides with variable repetition rate. Optics Express. 2005;**13**(12):4708-4716
- [4] Son Y, Yeo J, Moon H, Lim TW, Hong S, Nam KH, Yoo S, Grigoropoulos CP, Yang DY, Ko SH. Nanoscale electronics: Digital fabrication by direct femtosecond laser processing of metal nanoparticles. Advanced Materials. 2011;23(28):3176-3181
- [5] Ko SH, Park I, Pan H, Grigoropoulos CP, Pisano AP, Luscombe CK, Fréchet JMJ. Direct nanoimprinting of metal nanoparticles for nanoscale electronics fabrication. Nano Letters. 2007;7(7):1869-1877
- [6] Park S-H, Kim H-S. Flash light sintering of nickel nanoparticles for printed electronics. Thin Solid Films. 2014;**550**:575-581
- [7] Dreizin EL, Allen DJ, Glumac NG. Depression of melting point for protective aluminum oxide films. Chemical Physics Letters. 2015;**618**:63-65
- [8] Son Y, Yeo J, Ha CW, Lee J, Hong S, Nam KH, Yang D-Y, Ko SH. Application of the specific thermal properties of Ag nanoparticles to high-resolution metal patterning. Thermochimica Acta. 2012;**542**:52-56
- [9] Yeo J, Hong S, Lee D, Hotz N, Lee M-T, Grigoropoulos CP, Ko SH. Next generation non-vacuum, maskless, low temperature nanoparticle ink laser digital direct metal patterning for a large area flexible electronics. PLoS ONE. 2012;7(8):e42315
- [10] Pan H, , Ko SH, Grigoropoulos CP. Thermal sintering of solution-deposited nanoparticle silver ink films characterized by spectroscopic ellipsometry. Applied Physics Letters. 2008;93(23):234104

- [11] Ko SH, Pan H, Ryu SG, Misra N, Grigoropoulos CP, Park HK. Nanomaterial enabled laser transfer for organic light emitting material direct writing. Applied Physics Letters. 2008;93(15):151110
- [12] Pan H, Ko SH, Grigoropoulos CP. The solid-state neck growth mechanisms in low energy laser sintering of gold nanoparticles: A molecular dynamics simulation study. Journal of Heat Transfer. 2008;130(9):092404-092404-7
- [13] Kim SJ, Jang D-J. Laser-induced nanowelding of gold nanoparticles. Applied Physics Letters. 2005;86(3):033112
- [14] Hodak JH, Martini I, Hartland GV. Spectroscopy and dynamics of nanometer-sized noble metal particles. The Journal of Physical Chemistry B. 1998;102(36):6958-6967
- [15] Pan H, Ko SH, Grigoropoulos CP. The coalescence of supported gold nanoparticles induced by nanosecond laser irradiation. Applied Physics A. 2008;90(2):247-253
- [16] Paeng D, Lee D, Grigoropoulos CP. Characteristic time scales of coalescence of silver nanocomposite and nanoparticle films induced by continuous wave laser irradiation. Applied Physics Letters. 2014;105(7):073110
- [17] Lee Y, Zhang W. In mesoscopic simulation of heat transfer and fluid flow in laser powder bed additive manufacturing. International Solid Free Form Fabrication Symposium, Austin TX, USA; 2015. pp. 1154-1165
- [18] Paeng D, Yeo J, Lee D, Moon S-J, Grigoropoulos CP. Laser wavelength effect on laser-induced photo-thermal sintering of silver nanoparticles. Applied Physics A. 2015;120(4):1229-1240
- [19] Bieri NR, Chung J, Haferl SE, Poulikakos D, Grigoropoulos CP. Microstructuring by printing and laser curing of nanoparticle solutions. Applied Physics Letters. 2003;82(20):3529-3531
- [20] Choi TY, Poulikakos D, Grigoropoulos CP. Fountain-pen-based laser microstructuring with gold nanoparticle inks. Applied Physics Letters. 2004;85(1):13-15
- [21] Chung J, Bieri NR, Ko S, Grigoropoulos CP, Poulikakos D. In-tandem deposition and sintering of printed gold nanoparticle inks induced by continuous Gaussian laser irradiation. Applied Physics A. 2004;79(4):1259-1261
- [22] Chung J, Ko S, Bieri NR, Grigoropoulos CP, Poulikakos D. Conductor microstructures by laser curing of printed gold nanoparticle ink. Applied Physics Letters. 2004;84(5):801-803
- [23] Chung J, Ko S, Grigoropoulos CP, Bieri NR, Dockendorf C, Poulikakos D. Damage-free low temperature pulsed laser printing of gold nanoinks on polymers. Journal of Heat Transfer. 2005;127(7):724-732
- [24] Ko SH, Chung J, Pan H, Grigoropoulos CP, Poulikakos D. Fabrication of multilayer passive and active electric components on polymer using inkjet printing and low temperature laser processing. Sensors and Actuators A: Physical. 2007;134(1):161-168

- [25] Ko SH, Pan H, Grigoropoulos CP, Luscombe CK, Fréchet JM, Poulikakos D. All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles. Nanotechnology. 2007;18(34):345202
- [26] Ko SH, Pan H, Grigoropoulos CP, Luscombe CK, Fréchet JMJ, Poulikakos D. Air stable high resolution organic transistors by selective laser sintering of ink-jet printed metal nanoparticles. Applied Physics Letters. 2007;90(14):141103
- [27] Pan H, Hwang DJ, Ko SH, Clem TA, Fréchet JMJ, Bäuerle D, Grigoropoulos CP. High-throughput near-field optical nanoprocessing of solution-deposited nanoparticles. Small. 2010;6(16):1812-1821
- [28] Lee M-T, Lee D, Sherry A, Grigoropoulos CP. Rapid selective metal patterning on polydimethylsiloxane (PDMS) fabricated by capillarity-assisted laser direct write. Journal of Micromechanics and Microengineering. 2011;21(9):095018
- [29] Hong S, Yeo J, Kim G, Kim D, Lee H, Kwon J, Lee H, Lee P, Ko SH. Nonvacuum, maskless fabrication of a flexible metal grid transparent conductor by low-temperature selective laser sintering of nanoparticle ink. ACS Nano 2013;7(6):5024-5031
- [30] Son Y, Yeo J, Ha CW, Hong S, Ko SH, Yang D-Y. Fabrication of submicron-sized metal patterns on a flexible polymer substrate by femtosecond laser sintering of metal nanoparticles. International Journal of Nanomanufacturing 2. 2013;9(5-6):468-476
- [31] An K, Hong S, Han S, Lee H, Yeo J, Ko SH. Selective sintering of metal nanoparticle ink for maskless fabrication of an electrode micropattern using a spatially modulated laser beam by a digital micromirror device. ACS Applied Materials & Interfaces. 2014;6(4):2786-2790
- [32] Yang M, Chon M-W, Kim J-H, Lee S-H, Jo J, Yeo J, Ko SH, Choa S-H. Mechanical and environmental durability of roll-to-roll printed silver nanoparticle film using a rapid laser annealing process for flexible electronics. Microelectronics Reliability. 2014;54(12):2871-2880
- [33] Yeo J, Kim G, Hong S, Kim MS, Kim D, Lee J, Lee HB, Kwon J, Suh YD, Kang HW, Sung HJ, Choi J-H, Hong W-H, Ko JM, Lee S-H, Choa S-H, Ko SH. Flexible supercapacitor fabrication by room temperature rapid laser processing of roll-to-roll printed metal nanoparticle ink for wearable electronics application. Journal of Power Sources. 2014;246:562-568
- [34] Lee H, Hong S, Kwon J, Suh YD, Lee J, Moon H, Yeo J, Ko SH. All-solid-state flexible supercapacitors by fast laser annealing of printed metal nanoparticle layers. Journal of Materials Chemistry A. 2015;3(16):8339-8345
- [35] Suh YD, Jung J, Lee H, Yeo J, Hong S, Lee P, Lee D, Ko SH. Nanowire reinforced nanoparticle nanocomposite for highly flexible transparent electrodes: Borrowing ideas from macrocomposites in steel-wire reinforced concrete. Journal of Materials Chemistry C. 2017;5(4):791-798

- [36] Michael Z, Oleg E, Amir S, Zvi K. Laser sintering of copper nanoparticles. Journal of Physics D: Applied Physics. 2014;47(2):025501
- [37] Kwon J, Cho H, Eom H, Lee H, Suh YD, Moon H, Shin J, Hong S, Ko SH. Low-temperature oxidation-free selective laser sintering of Cu nanoparticle paste on a polymer substrate for the flexible touch panel applications. ACS Applied Materials & Interfaces. 2016;8(18):11575-11582
- [38] Suh YD, Kwon J, Lee J, Lee H, Jeong S, Kim D, Cho H, Yeo J, Ko SH. Maskless fabrication of highly robust, flexible transparent Cu conductor by random crack network assisted Cu nanoparticle patterning and laser sintering. Advanced Electronic Materials. 2016;**2**(12)
- [39] Pan H, Ko SH, Misra N, Grigoropoulos CP. Laser annealed composite titanium dioxide electrodes for dye-sensitized solar cells on glass and plastics. Applied Physics Letters. 2009;94(7):071117
- [40] Pan H, Misra N, Ko SH, Grigoropoulos CP, Miller N, Haller EE, Dubon O. Melt-mediated coalescence of solution-deposited ZnO nanoparticles by excimer laser annealing for thin-film transistor fabrication. Applied Physics A. 2009;94(1):111-115
- [41] Lee D, Pan H, Ko SH, Park HK, Kim E, Grigoropoulos CP. Non-vacuum, single-step conductive transparent ZnO patterning by ultra-short pulsed laser annealing of solutiondeposited nanoparticles. Applied Physics A. 2012;107(1):161-171
- [42] Pan H, Lee D, Ko SH, Grigoropoulos CP, Park HK, Hoult T. Fiber laser annealing of indium-tin-oxide nanoparticles for large area transparent conductive layers and optical film characterization. Applied Physics A. 2011;104(1):29-38
- [43] Kang B, Han S, Kim J, Ko S, Yang M. One-step fabrication of copper electrode by laserinduced direct local reduction and agglomeration of copper oxide nanoparticle. The Journal of Physical Chemistry C. 2011;115(48):23664-23670
- [44] Lee D, Paeng D, Park HK, Grigoropoulos CP. Vacuum-free, maskless patterning of Ni electrodes by laser reductive sintering of NiO nanoparticle ink and its application to transparent conductors. ACS Nano. 2014;8(10):9807-9814
- [45] Kang B, Ko S, Kim J, Yang M. Microelectrode fabrication by laser direct curing of tiny nanoparticle self-generated from organometallic ink. Optics Express. 2011;19(3):2573-2579
- [46] Liu Y-K, Lee M-T. Laser direct synthesis and patterning of silver nano/microstructures on a polymer substrate. ACS Applied Materials & Interfaces. 2014;6(16):14576-14582

IntechOpen

IntechOpen