High resolution selective multilayer laser processing by nanosecond laser ablation of metal nanoparticle films

Seung H. Ko, Heng Pan, David J. Hwang, Jae-woon Chung, Sangil Ryu, and Costas P. Grigoropoulos

Laser Thermal Laboratory, Department of Mechanical Engineering, University of California, Berkeley, California 94720-1740, USA

Dimos Poulikakos

Laboratory of Thermodynamics in Emerging Technologies, Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland

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Ablation of gold nanoparticle films on polymer was explored using a nanosecond pulsed laser, with the goal to achieve feature size reduction and functionality not amenable with inkjet printing. The ablation threshold fluence for the unsintered nanoparticle deposit was at least ten times lower than the reported threshold for the bulk film. This could be explained by the combined effects of melting temperature depression, lower conductive heat transfer loss, strong absorption of the incident laser beam, and the relatively weak bonding between nanoparticles. The ablation physics were verified by the nanoparticle sintering characterization, ablation threshold measurement, time resolved ablation plume shadowgraphs, analysis of ablation ejecta, and the measurement and calculation of optical properties. High resolution and clean feature fabrication with small energy and selective multilayer processing are demonstrated. © 2007 American Institute of Physics. [DOI: 10.1063/1.2802302]

I. INTRODUCTION

Pulsed laser ablation (PLA) has been extensively studied in the past as an effective technique for the direct patterning of thin metal films. Owing to precise localized ablation for a wide variety of materials and the fully data driven and maskless nature of the PLA process, it has emerged as a viable technique in applications such as circuit patterning and trimming, mask repair, etc. The nanosecond PLA process starts with absorption of the irradiated laser beam, leading to temperature increase and the subsequent melting and vaporization. Depending on the fluence, the vaporized plume or plasma exerts a recoil pressure, expelling outward or even splashing the melt pool that tends to resolidify at the periphery of the crater. For high quality patterning, it is desirable to minimize these effects. In view of these requirements, ultrashort (femto- or picosecond) pulsed laser ablation has successfully demonstrated precise crater drilling due to the very short time scales involved in the ablation process that tends to suppress, although not completely eliminate, thermal transfer. It is noted that even in the ultrafast laser processing of metals, sophisticated beam delivery algorithms and shaping have been used to mitigate melting effects.

In this study, self-assembled monolayer (SAM) protected gold nanoparticle (1–3 nm diameter) film on polyimide was ablated using frequency doubled Nd:YAG (YAG denotes yttrium aluminum garnet) nanosecond laser (3–5 ns pulse width) for the purpose of trimming a drop on demand (DOD) ink-jet printed electrical microconductor for flexible electronics. Nanoparticles are used to exploit the significant depression of the melting temperature compared to bulk gold (1063 °C) due to the thermodynamic size effect. This implies that the nanoparticles can be sintered at reduced temperature that is compatible with flexible polymer substrates. Hexanethiol surface monolayer prevents agglomeration in various organic solvents, allowing printing of the nanoparticle solution without clogging at the ink-jet nozzle. Therefore, employment of a cost-effective DOD inkjet printing process combined with nanoparticles instead of conventional integrated circuit (IC) fabrication is expected to open new opportunities in the manufacture of flexible electronics. However, the typical resolution of printing processes is of the order of 50–100 μm, motivating the development of hybrid schemes that utilize tightly focused laser irradiation to achieve higher feature resolution and improved functionality. With this goal in mind, the characteristics of nanosecond laser ablation of nanoparticle film were explored and the detailed ablation physics were discussed in the current study based on experimental observations. Finally, the unique ablation characteristics of nanoparticle film were applied to demonstrate high resolution and clean feature fabrication with small energy as well as selective multilayer processing on a polymer substrate.

II. EXPERIMENT

Gold nanoparticles were synthesized by a chemical two-phase method to obtain 1–3 nm sized nanoparticles. Unsintered and sintered nanoparticle film on polymer substrate were prepared and ablated to compare the respective ablation characteristics. Several experiments were carried out to understand the nanoparticle film ablation physics. The sintering process was interrogated by monitoring the resistivity, reflectivity, and weight loss dependence on sintering temperature. Ablation crater profiles were scanned using an atomic force microscope (AFM) to calculate the ablation threshold. Time
resolved shadowgraph images of the ablation plume were taken to observe the transient behavior of the ablation process in conjunction with microscopy analysis of collected ejecta. Finally, optical properties and thermal properties of nanoparticle film were discussed using measurements and calculation.

A. Nanoparticle synthesis and characterization

The gold nanoparticles were prepared by the two-phase reduction method reported by Brust et al.\textsuperscript{17} Aqueous metal salts (HAuCl\textsubscript{4}) were mixed in a toluene solution containing long-chain alkylammonium surfactants to form a two-phase system. A 1.5 g of tetroactylammonium bromide (C\textsubscript{32}H\textsubscript{68}BrN) was mixed with 80 ml of toluene and added to 0.31 g of hydrogen tetrachloroaurate (III) hydrate (HAuCl\textsubscript{4}·xH\textsubscript{2}O) in 25 ml of de-ionized (DI) water. Vigorous stirring transferred the metal salt (AuCl\textsubscript{4}⁻) into the organic phase (toluene) and the aqueous phase was removed. A measured quantity of capping agent, a long-chain thiol (hexanethiol), was added to the gold solution while stirring. A reducing agent, sodium borohydride (NaBH\textsubscript{4}), mixed in 25 ml of water was then added fast into the organic phase over approximately 10 s to nucleate nanocrystals. The mixture reacted at room temperature for 3.5 h. The toluene was removed with a rotary evaporator and the leftover black particles were suspended in ethanol and sonicated briefly. The particles were washed with ethanol and acetone and then dried in air. The size of synthesized nanoparticles is distributed from 1 to 3 nm as measured using a transmission electron microscope (TEM) [Fig. 1(a)]. Monolayer-protected gold nanoparticles [Fig. 1(c)] are suspended in alpha-terpineol with 10% in weight [Fig. 1(b)]. Figure 1(d) represents the schematic configuration of the SAM protected nanoparticles.

B. Unsintered and sintered nanoparticle film ablation characterization

A SAM protected nanoparticle film (hereafter referred to as “unsintered nanoparticle film”) was prepared by spin-coating gold nanoparticles suspended in alpha-terpineol on polyimide film to ensure uniform thickness and subsequently dried at 100 and 120 °C for 2 h to vaporize the solvent. The resulting nanoparticle film (about 2.3 μm thick) was ablated using an infinity-corrected long working distance objective lens that focuses the laser beam and at the same time images the sample surface in reflected light. The incident laser pulse energy after the objective lens was varied from 0.4 to 40 μJ to ablate prepared nanoparticle films. To investigate the effect of thermal sintering on the ablation of the nanoparticle film, the unsintered nanoparticle film was additionally heated at 160 °C for 2 h and the resulting sintered nanoparticle film (1 μm thick) was then ablated.

Unsintered and sintered nanoparticle films were placed on the three axis translating and tilting micromachining workstation including the \textit{in situ} imaging setup for laser ablation shown in Fig. 2. An infinity-corrected long working distance objective lens was used to focus the frequency doubled Nd:YAG nanosecond laser (532 nm wavelength, 5 ns pulse width) and image the sample surface with a zoom lens and a charge coupled device (CCD) camera. The white light illumination was combined with the laser beam using a dichroic mirror (DM). For finer adjustment of the laser beam energy, a half wave plate (HWP) and a polarizing beam splitter (PBS) were employed. The energy of the pulsed laser after the objective lens was varied from 0.4 to 40 μJ to ablate the prepared nanoparticle films.

The diameter and depth of the ablation craters of unsintered and sintered gold nanoparticle film were measured using an AFM and were used to calculate the ablation thresh-
old. Time resolved images of the ablation ejecta from both unsintered and sintered nanoparticle film were taken by shadowgraph imaging method with nitrogen laser pumped dye laser illumination (440 nm wavelength, 10 ns pulse width). Another CCD camera was placed parallel to the sample surface. The bandpass filter in front of this CCD camera blocked the scattering of ablation laser beam (532 nm) and accepted only the illumination laser beam (440 nm). The time delay between the ablation laser (pump beam) and the illumination laser (probe beam) was set by delay generators, and the actual delay was measured by a photodetector connected to an oscilloscope. The delay time was varied from 1 to 12 μs. The captured images were processed by subtracting the background noise to improve clarity. The ablation ejecta from unsintered and sintered nanoparticle film were collected on a quartz substrate placed 1 mm above the ablation surface. Images of collected ejecta were taken by a scanning electron microscope (SEM), as well as a dark field optical microscope.

II. RESULTS AND DISCUSSION

Nanomaterials exhibit remarkable specific properties due to large surface area to volume ratio, large surface energy, and the spatial confinement effect. Unsintered nanoparticle film shows several interesting characteristics such as much cleaner and higher resolution ablation craters compared with the sintered nanoparticle film. Figure 3 shows a nanosecond laser ablation crater [Fig. 3(a)] and a trench [Fig. 3(c)] of nanosecond laser ablation of unsintered nanoparticle film, and a crater [Fig. 3(b)] and a trench [Fig. 3(d)] of nanosecond laser ablation of sintered nanoparticle films. Ablation craters of unsintered nanoparticle film are clean and have abrupt edge profiles, while craters punched into sintered nanoparticle film have rather messy rims causing poor line edge resolution. The physics of the unique ablation characteristics of the unsintered nanoparticle film are explored chiefly via comparison with the ablation of sintered nanoparticle film. Potential utilization of these characteristics for selective multilayer processing and high resolution metal patterning is demonstrated.

A. Nanoparticle sintering characterization

The reflectivity, weight loss, and resistivity of the gold nanoparticle film were measured as a function of temperature at the heating rate of 5 °C/min. Both the resistivity (indi-
cated by the black line in Fig. 4) and the reflectivity at the 514.5 nm probe laser wavelength (indicated by the blue line in Fig. 4) of the gold nanoparticle film changed sharply at about 180 °C. In addition, thermogravimetry analysis (TGA) verified that about 17% of weight loss (indicated by the red line in Fig. 4, measured at 5 °C/min by Seiko Instruments SSC 5200 TG/DTA 220 in air environment) occurred at almost the same temperature range. This 17% weight loss matches well with the theoretical mass percentage of the SAM on gold nanoparticles with 3 nm diameter. Accordingly, it is inferred that the surface monolayer (hexanethiol) starts to desorb from the nanoparticle at about 180 °C, initiating the nanoparticle sintering.

In addition, the resistivity of ink-jet printed gold nanoparticle lines (1 cm long, 100 μm wide) was measured at room temperature, after sintering on a hot plate for 1 hour at each temperature of interest. The resistivity was calculated from $\rho = R \cdot A / L$, where $R$, $A$, and $L$ are the resistance, cross sectional area, and length of the test sample, respectively. The cross sectional area ($A$) was deduced from AFM scanning data and the resistance ($R$) was measured with a microneedle probe station. As shown in Fig. 4, the resistivity (indicated by the black line) starts to decrease at 130–140 °C. Based on these results, unsintered nanoparticle films were prepared by heating at 100 and 120 °C for 2 h.
B. Nanoparticle film ablation threshold (low ablation threshold)

Figure 5 shows crater profiles of unsintered [(a)–(c)] and sintered (d) nanoparticle film ablated by nanosecond laser. In Fig. 5(a), the ablation depth increases almost linearly with the number of laser pulses, while the ablation radius does not change significantly with the number of laser pulses except in the case of 600 pulses. The ablation radius increases with the pulse energy, as shown in Fig. 5(b). Note that the elevated rim structure that is often observed in metal film craters ablated by nanosecond lasers is absent in the ablation of unsintered nanoparticle film that produces very clean, Gaussian-type ablation profiles at relatively low laser fluences. When this ablated unsintered nanoparticle film was additionally sintered at higher temperature to obtain an electrically conductive film, the crater morphology did not change significantly, although the film thickness decreased by about two times due to desorption and subsequent evaporation of the SAM followed by possible compaction of nanoparticles due to sintering [Fig. 5(c)].

When the sintered nanoparticle film was subjected to the laser fluence of 0.17 J/cm², a granulated morphology was observed [Fig. 5(d), dotted line with circle symbols for eight laser shots]. Since the sintered nanoparticle film morphology and structure are similar to a solid metal film, melting occurs possibly with minimal evaporation followed by resolidification to the granulated morphology. Upon irradiation by multiple laser pulses [Fig. 5(d), dotted line, 600 shots], the polyimide protruded due to cumulative thermal damage and the sintered nanoparticle film cracked. Similar swelling has been reported for polyimide exposed to direct laser irradiation near the ablation threshold. However, in the present case, the laser irradiation is absorbed by the sintered nanoparticle film inducing thermal damage to the polyimide film. Note that at the same laser fluence [Fig. 5(a)], irradiation of multiple laser pulses on the unsintered nanoparticle film did not induce deformation of the polyimide film due to the low thermal conductivity of the unsintered nanoparticle film.

When the incident peak fluence at the laser center was 1.4 J/cm² (i.e., higher than the reported ablation threshold fluence of gold film at 532 nm), a crater profile alike the typically observed in metal film ablation via nanosecond laser irradiation was obtained [Fig. 5(d), solid line, eight laser shots]. The elevated rim profile due to melt expulsion and splashing of the molten pool can be clearly seen. Ablative material removal of sintered nanoparticle film occurred at incident peak fluence higher than 0.7–0.9 J/cm². Below 0.7–0.9 J/cm², the sintered nanoparticle film melted and was then pulled radially outward by capillary forces to expose the underlying polyimide film, although the net material removal was insignificant according to the volumetric data derived from the AFM images.

To determine the ablation threshold of the unsintered nanoparticle film, the unsintered gold nanoparticle film was ablated by varying the incident energy and number of irradiated laser pulses. As shown in Fig. 6, the ablation radius \( r_A \) measured from the AFM images increases with the incident fluence. Assuming a Gaussian incident laser beam profile, the ablation threshold fluence \( F_A \) is related to the ablation radius \( r_A \) (Ref. 24) that is measured from the AFM image by

\[
r_A = \frac{w_0}{\sqrt{2}} \sqrt{\ln \left( \frac{F_{\text{peak}}}{F_A} \right)},
\]

where \( w_0 \) is the beam radius to \( 1/e^2 \) in intensity compared to peak-on-axis beam fluence. The corresponding peak-on-axis beam fluence was calculated using \( F_{\text{peak}} = 2E/\pi w_0^2 \) from the measured incident pulsed energy \( E \). Outside the ablation spot, no significant damage was observed, as, for example, shown in Figs. 3(a) and 3(c). However, Fig. 6 indicates that the ablation radius slightly increases with the number of irradiated laser pulses, implying nonablating modification of the sample material that decreases the ablation threshold. This multiple pulse effect (also called “incubation effect” or “accumulation effect”) can be quantified by the following equation:

\[
F_{A,N} = F_A N^{S-1}.
\]

Here, the multiple pulse ablation threshold fluence \( F_{A,N} \) decreases with the number of incident laser pulses, \( N \), when the material dependent accumulation coefficient \( S \) is lower than 1. Combining the above equations, the equation for curve fitting in Fig. 6(a) can be obtained as follows:

\[
r_{A,N} = \frac{w_0}{\sqrt{2}} \sqrt{\ln \left( \frac{F_{\text{peak}}}{F_A N^{S-1}} \right)}.
\]

According to curve fitting, the single shot ablation threshold fluence and the accumulation coefficient were obtained as 0.03 J/cm² and 0.92, respectively. Note that the typical metal film ablation threshold fluence using a nanosecond laser at visible wavelength lies within the range of 1–10 J/cm², and the ablation threshold fluence of 0.5 J/cm² was reported at the laser wavelength of 532 nm for deposited gold film.

The different ablation crater shapes and thresholds signify that unsintered and sintered nanoparticle films have dif-
different material structures. Nanoparticles in unsintered nanoparticle films are separated by voids or SAM and are therefore held together by weak physical van der Waals forces (so-called “soft agglomerates”) compared with sintered nanoparticle film that has strong polycrystalline metal bonding.

C. Time resolved shadowgraph imaging and collection of ejecta (loosely bonded nanoparticle film)

Figure 7 shows time resolved shadowgraph images of the ablation plume ejection from the sintered nanoparticle film [Figs. 7(a) and 7(d)] and from the unsintered nanoparticle film [Figs. 7(b) and 7(c)] over the time period of 1–12 μs. While micrometer sized molten droplets were ejected from the sintered nanoparticle film at a velocity of 40 m/s [Fig. 7(d)], unsintered nanoparticle ablation produced mist jetlike ejecta [Fig. 7(c)] at almost the same velocity but exhibiting good directionality. Note that mist jetlike ejection plume was often observed in the ablation of organic materials such as photodecomposable polymer, suggesting that SAM may play a similar role during the ablation of the nanoparticle film. The unsintered nanoparticles are protected by organic surface monolayer and are loosely bonded like decomposed polymer chains.

Figure 8 shows SEM and dark field optical microscope images of laser ablation ejecta collected on a quartz substrate placed at 1 mm above the ablation surface. Here, the pulsed laser beam was scanned with the quartz substrate and the target specimen stationary, so that ejecta were collected in a horizontal line, as shown in Fig. 8(b). However, the ejection process from the sintered nanoparticle film is intermittent, as shown in Fig. 7(a), and the collected particles in Fig. 8(a) are widely spread, relatively big molten drops (~several micrometers) and exfoliated film fragments. On the contrary, the ablation of unsintered nanoparticle film produced 5 ~50 nm aggregates [SEM pictures, Fig. 8(b) inset], including agglomerates that grew at the expense of smaller molten nanoparticles [Fig. 8(b)]. These products are correlated to the mist jet recorded in Fig. 7(b). The brightness of unsintered nanoparticle film changed upon heating above 130 ~140 °C, signifying presence of not only molten nanoparticles but also unsintered nanoparticles covered by SAM.

It is noted that the gas composition, background pressure, and convective force are important factors for obtaining clean ablation. When the background pressure is high, the ablated ejecta are redeposited onto the surface near the ablation spot due to interaction with the gas environment. When the ablation was done in vacuum, the ejecta redeposition could be eliminated. A similar effect could be seen when laminar flow was applied on the ablation spot to efficiently sweep away the ablation debris.

D. Nanoparticle optical properties (efficient energy coupling)

If a metal particle is smaller than the mean free path of conduction electrons in the bulk metal, the energy deposition is dominated by the carrier collisions with the particle boundary. One way to consider this behavior is by splitting the dielectric function into a free-electron term and a bound-electron term. Only the free-electron term is modified by increasing the Drude theory damping constant because of the
increased number of collisions at the particle boundary. This is valid under the assumption that electrons are diffusely reflected at the boundary. The average dielectric function may be calculated by the following effective medium theory, where $e$ and $e_m$ are the dielectric functions of the particle and the matrix medium, respectively, and $f$ is the volume fraction of inclusions:

$$e_{av} = e_m \left[ 1 + \frac{3f(e - e_m)}{e + 2e_m} \right] \left[ 1 - f(e - e_m) \right].$$

Figure 9 shows (a) the normal incidence reflectance and (b) the optical absorption depth for 200–1200 nm range. The nanoparticle film is assumed to be closely packed with the volume fraction of 6.5% in the air. The nanoparticles are of 2 nm diameter with 1 nm SAM shell. Note the dip indicated by the arrow in the neighborhood of 520 nm in Fig. 9(b). The theoretical calculations matched well with the experimental measurements ($\rho$: 0.058, $l$: 150 nm) at the wavelength of 514 nm.

Maxwell-Garnett effective medium theory calculation with conduction electron mean free path correction revealed that the nanoparticle thin film was less reflective and strongly absorbing (reflectance ($\rho$): 0.06, absorption depth ($l$): 251 nm) compared with the bulk gold thin film ($\rho$: 0.64, $l$: 19.3 nm) due to electron scattering. In addition, enhanced electric fields between nanoparticles could contribute to more efficient energy deposition. In summary, the incident laser pulse energy is efficiently absorbed by nanoparticles due to the lower reflectance and strong absorption. This is because of the aforementioned strong absorption peak near the 520 nm wavelength that cannot be observed in bulk material due to surface plasmon oscillation modes of conduction electrons in the nanoparticles.

E. Nanoparticle thermal properties (lower thermal diffusion)

Besides efficient energy deposition, the deposited energy is more confined to the laser focal spot due to reduced thermal diffusion in the nanoparticle thin film. The low thermal conductivity in nanostructured materials is well known in the thermoelectric energy conversion field. The nanosystem thermal conductivity is determined by the presence of the interface that induces phonon reflection (Kapitza resistance) or phonon scattering. Estimates of the effective thermal conductivity of nanoparticle composite medium with specific volume fraction of alkanethiol are lower than the bulk material counterpart. However, the thermal conductivity of the nanosystem is not simple but governed by the presence of the nanoparticle/matrix interface. It is reported that the thermal conductance of AuPd nanoparticles stabilized by alkanethiol is around 5 MW/m²K which is at least two or three orders of magnitude smaller than bulk film. Upon reaching the interface, a phonon will either transmit or reflect as dictated by a transmission probability that may be described by the acoustic mismatch model (AMM) and the diffuse mismatch model (DMM). Bulk solids exhibit continuous vibrational spectra in contrast to surface monolayers and nanoparticles that possess discrete vibrational spectra that couple with low overall transmission probability. Furthermore, since the alkanethiol molecules weakly interact...
with each other, it is expected that the transmission of transverse phonons will be poor. For these reasons, it is anticipated that the thermal conductance of the thiol stabilized nanoparticles will be very low.33

F. High resolution feature fabrication and selective multilayer processing

Based on the physical understanding of nanoparticle film ablation, the low ablation threshold could be exploited to achieve high resolution feature fabrication and selective multilayer processing. Recall that laser ablation of sintered film [Fig. 3(d)] showed elevated rim profile due to melt expulsion, while laser ablation of unsintered nanoparticle film [Fig. 3(c)] yielded clean features. Figure 10 shows submicron lines [full width at half maximum (FWHM): 400–800 nm] with 3 μm pitch. The ablated and sintered lines were highly electrically conductive and isolated from each other. Note that the ink-jet printing resolution is 50–100 μm, and that production of such small features would require photolithography. The size of the conductive positive features can be reduced significantly with higher magnification focusing lens and even sub-100-μm features will be possible with near-field scanning optical microscopy (NSOM) based ablation scheme.

Laser ablation of unsintered gold nanoparticle film not only showed a much cleaner ablation profile but also exhibited lower ablation threshold than the sintered gold nanoparticle film. This ablation threshold difference can be used for the selective ablation of multilayer structures. In principle, selective ablation in multilayer can be done by placing the laser focal point exactly on the target layer, expecting that the underlying layer would be outside the depth of focus and, hence, irradiated by laser light intensity below the damage threshold. However, this approach would be practically difficult since our target metal layer thickness is of the order of several tens of nanometers and the dielectric layer thickness is also very small. Consequently, very small depth of focus would be needed proportional to the multilayer separation distance. Therefore, it is very difficult to ablate only the top layer selectively by adjusting the depth of focus placement without affecting the underlying conductor layer, especially when the interlayer is a transparent material and the separation between the conductor layers is submicron. On the contrary, the ablation threshold difference between the laser sintered and unsintered gold nanoparticle solution enables effective and robust multilayer processing. Figure 11 shows successful selective multilayer processing of ink-jet printed gold nanoparticle suspension deposits. The basic structure is the same with a crossover capacitor except that the upper line is not sintered. A lower level line (printed in vertical direction) was ink-jet printed and sintered by the continuous laser irradiation to yield a high electrical conductivity line. A poly-4-vinylphenol (PVP) dielectric layer was ink-jet printed and the upper level gold nanoparticle solution was printed on top of the PVP layer. Finally, pulsed laser radiation was applied to selectively ablate the upper unsintered gold nanoparticle solution line without inflicting damage to the lower level.
gold line. Subsequently, the upper gold nanoparticle line can be laser sintered to produce a conductor line.

IV. CONCLUSION

In conclusion, ablation of gold nanoparticle films on polymer substrate was explored using a frequency doubled Nd:YAG nanosecond laser, with the goal to achieve feature size reduction and functionality. When the unsintered nanoparticle film was ablated and then thermally sintered to a continuous film, low ablation threshold (0.03 J/cm²) and the clean crater morphology without an elevated rim structure were observed.

During the laser ablation of unsintered nanoparticle film, the incident laser pulse energy is first absorbed by nanoparticles more efficiently due to smaller reflectance and strong absorption near the 520 nm wavelength due to surface plasmon oscillation modes of conduction electrons in the nanoparticles. In addition, enhanced electric fields between nanoparticles could contribute to more efficient energy deposition. Beside efficient energy absorption, the absorbed energy is more confined to the laser focal spot due to reduced thermal diffusion in the nanoparticle thin film. The efficiently deposited energy with small conduction loss induces nanoparticle melting at very low energy level due to the thermodynamic size effect and is transferred to SAM or residual particle melting at very low energy level due to the thermal energy is more confined to the laser focal spot due to reduced particles could contribute to more efficient energy deposition. Beside efficient energy absorption, the absorbed energy is more confined to the laser focal spot due to reduced thermal diffusion in the nanoparticle thin film. The efficiently deposited energy with small conduction loss induces nanoparticle melting at very low energy level due to the thermodynamic size effect and is transferred to SAM or residual solvent to induce evaporation. The melting temperature depression enables ablation at much lower laser energy than needed for the respective bulk material. Upon reaching the nanoparticle sintering temperature (130–140 °C), the SAM desorbs and becomes volatile. At this stage, molten nanoparticles agglomerate to bigger particles that are expelled by the pressure built up from the volatile species expansion such as desorbed SAM and trapped air gas. In addition, due to the presence of SAM, nanoparticles are held together by weak physical van der Waals force compared with the strong polycrystalline metal bonding in sintered nanoparticle film material. Therefore, the expulsion is enhanced by the relatively weak bonding between the nanoparticles. These combined effects contribute to the low ablation threshold and clean ablated feature profile in unsintered nanoparticle film.

High resolution (FWHM: 400–800 nm) and clean feature fabrication was demonstrated with small energy enabling multilayer processing by selective pulsed laser ablation by differential ablation threshold (SPLA-DAT). The possibility of utilizing high frequency nanosecond laser and combination of nanoparticle direct nanoimprinting could make this method attractive in flexible electronics manufacturing.

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