Nanosecond laser ablation of gold nanoparticle films

Seung H. Ko, Yeonho Choi, David J. Hwang, and Costas P. Grigoropoulos
Laser Thermal Laboratory, Department of Mechanical Engineering, University of California, Berkeley, California 94720-1740

Jaewon Chungb)
Department of Mechanical Engineering, Korea University, Seoul 136-713, South Korea
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 self-assembled monolayer protected gold nanoparticle films on polyimide was explored using a nanosecond laser. When the nanoparticle film was ablated and subsequently thermally sintered to a continuous film, the elevated rim structure by the expulsion of molten pool could be avoided and the ablation threshold fluence was reduced to a value at least ten times lower than the reported threshold for the gold film. This could be explained by the unusual properties of nanoparticle film such as low melting temperature, weak bonding between nanoparticles, efficient laser energy deposition, and reduced heat loss. Finally, submicron lines were demonstrated. © 2006 American Institute of Physics. [DOI: 10.1063/1.2360241]

Nanosecond pulsed laser ablation has been extensively studied as an effective technique for fully data driven and mask-less direct patterning due to precisely localized ablation for a wide variety of materials. However, for materials with high thermal diffusivity such as metals, damage-free patterning can only be achieved with femtosecond pulses.1

In this study, alkanethiol self-assembled monolayer (SAM) protected gold nanoparticle film on polyimide substrate was ablated using a frequency doubled neodymnium doped yttrium aluminum garnet nanosecond laser (3–5 ns pulse width). The purpose of this study is to improve functionality and enhance feature resolution of drop-on-demand ink-jet printed electrical microconductors (usually limited to 50–100 μm resolution)2–5 for flexible electronics in lieu of conventional integrated chip fabrication processing. Nanoparticles are used to exploit the significant melting temperature depression compared to bulk gold (1063 °C) due to the thermodynamic size effect.6 This implies reduced and hence plastic-compatible processing temperature. With this goal in mind, nanosecond laser ablation of nanoparticle film was explored in the current study.

SAM protected gold nanoparticles were synthesized using a two-phase reduction method.5,7 SAM is critical for nanoparticles because it controls the size of the nanoparticles in addition to enhancing long term stability and achieving favorable optical properties through Au-thiol chemistry. The size of synthesized nanoparticles is distributed over the range of 1–3 nm as measured by transmission electron microscopy. The nanoparticle sintering characteristics were investigated at various temperatures. Both electrical conductivity and reflectivity were increased past the range of 130–140 °C where the SAM desorbs and evaporates away (verified from thermogravimetry analysis). Based on these results, a nanoparticle film (hereafter referred to as “unsintered nanoparticle film”) was prepared by spin coating gold nanoparticles suspended in alpha terpineol on polyimide film and subsequently dried at 120 °C. The resulting nanoparticle film (~2.3 μm) was ablated using an infinity-corrected long working distance objective lens at the incident laser pulse energy of 0.4–40 μJ.

Figure 1(a) shows crater profiles of unsintered nanoparticle film ablated at 0.17 J/cm2 fluence (Fpeak, peak-on-axis beam fluence). Notice the absence of elevated rim structure that is often observed in metal film craters [Figs. 1(b) and 1(c)] ablated by nanosecond lasers and also the clean, Gaussian-shaped ablation profile at low laser fluence. To investigate the effect of sintering on the ablation of the nanoparticle film, the unsintered nanoparticle film was additionally heated at 160 °C to obtain highly electrically conductive film and the resulting sintered nanoparticle film (~1 μm) was then ablated. Incident laser energy higher than 0.15–0.2 μJ produced granulated morphology instead of ablation crater recess as shown in Fig. 1(b). Since the sintered nanoparticle film morphology and structure become similar to a metal film, melting occurs possibly with minimal evaporation and is followed by redistribution and resolidification to the granulated morphology. At incident peak fluence of 1.4 J/cm2, a typical crater profile produced via nanosecond laser ablation of metal film was obtained [Fig. 1(c)]. The elevated rim profile due to melt expulsion and splashing of the molten pool can be clearly seen in Fig. 1(c). 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 was melted and pulled outward to expose the underlying polyimide film. The ablation threshold of the unsintered nanoparticle film was calculated from atomic force microscopy (AFM) images taken at different irradiated laser pulse numbers and energy levels (Fig. 2). Assuming a Gaussian incident laser beam profile, the ablation threshold fluence FA is related to the ablation radius ra by

\[ F_A = \frac{2\pi r_a}{\lambda} \]
chemical properties such as low melting temperature, desorption and thermal diffusion, as well as to physical and mechanism, attention should be paid to the laser energy absorbed under the unsintered nanoparticle film laser ablation process.1 To investigate whether this ablation phenomenon applies to other nanoparticle systems, a film of polyvinylpyrrolidone-capped silver nanoparticles, synthesized by the Poyol method,9 was ablated. Crater profiles for gold could be observed, while the ablation threshold fluence and accumulation coefficient were 0.03 J/cm² and 0.92, respectively. Note that the ablation threshold fluence and accumulation coefficient were measured as 0.03–0.08 J/cm². The fitting curves were obtained from Eq. (1) for each case.

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

where \( F_{\text{peak}} = 2E/(\pi w_0^2) \). Multiple pulse effect was considered by substituting \( F_A \) in Eq. (1) by \( F_{A,N} = F_A N^6 e^{-1.8} \).

According to curve fitting, the single shot ablation threshold fluence and accumulation coefficient were 0.03 J/cm² and 0.92, respectively. Note that the ablation threshold is at least one order lower than the reported ablation threshold for deposited gold (0.5 J/cm²) and other metal films (1–10 J/cm²) for nanosecond laser irradiation at visible wavelength.19 To investigate whether this ablation phenomenon applies to other nanoparticle systems, a film of polypyrrolidone-capped silver nanoparticles, synthesized by the Poyol method,7 was ablated. Crater profiles for both sintered and unsintered nanoparticle silver films similar to gold could be observed, while the ablation threshold fluence of unsintered film was measured as 0.03–0.08 J/cm².

The different ablation thresholds and crater morphologies signify that the unsintered nanoparticle film exhibits different ablation behaviors from sintered nanoparticle film. To understand the unsintered nanoparticle film laser ablation mechanism, attention should be paid to the laser energy absorption and thermal diffusion, as well as to physical and chemical properties such as low melting temperature, different bonding, optical, and thermal characteristics.

Nanomaterials exhibit remarkable properties departing from the bulk material counterparts due to the large surface area to volume ratio, high surface energy, and spatial confinement. The incident laser pulse energy is first absorbed by nanoparticles more efficiently due to lower reflectance and strong absorption. Gold nanoparticles exhibit a 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.10 Maxwell-Garnett effective medium theory calculation with conduction electron mean free path correction11 revealed that nanoparticle thin film was less reflective and strongly absorbing (reflectance (ρ): 0.06 and absorption depth (l): 251 nm) compared with the bulk gold thin film (ρ: 0.64 and l: 19.3 nm) due to electron scattering.12 The theoretical calculations matched well the experimental measurements (ρ: 0.058 and l: 150 nm) at the wavelength of 514 nm. In addition, enhanced electric fields between nanoparticles could contribute to more efficient energy deposition mechanism.12 Besides the 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 of nanostructured materials is well known in the thermoelectric energy conversion area.13 The nanosystem thermal conductivity is determined by the presence of the interface that induces phonon reflection (Kapitza resistance) or phonon scattering. It is reported that AuPd nanoparticles stabilized by alkanethiol have very small thermal conductance (5 MW/m²K) due to the huge vibrational mismatch.
between the nanoparticle solid core and the surface monolayer. The efficiently deposited energy that experiences lower conduction loss induces nanoparticle melting at very low energy level due to thermodynamic size effect. Heat is then transferred to the SAM or residual solvent inducing evaporation. The melting temperature depression enables ablation driven by material melting and vaporization at much lower laser energy than bulk. Upon reaching the nanoparticle sintering temperature (130–140 °C), the SAM desorbs and becomes volatile. At this stage, molten nanoparticles agglomerate to bigger molten particles that are expelled by the pressure built-up from the volatile species expansion such as desorbed SAM, residual organic solvent, 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. These combined effects contribute to the low ablation threshold and clean ablation profile.

Scanning electron microscopy (SEM) and dark field optical microscope images of laser ablation ejecta collected on a quartz substrate placed at 1 mm gap above the ablation surface are shown in Fig. 3. The ejecta from sintered nanoparticle film consisted of big molten drops (approximately in micrometers) and exfoliated film fragments. On the contrary, the laser ablation of unsintered nanoparticle film produced 5–50 nm aggregates, including the agglomerates that grew at the expense of smaller molten nanoparticles. The brightness of this deposit changed upon heating above the sintering temperature of 130–140 °C, signifying that the ejecta from contain not only molten nanoparticles but also unsintered nanoparticles with SAM.

Based on the nanoparticle film laser ablation, Au positive lines were fabricated. Figure 4 shows how this technique can be applied to improve the quality of ablation features. Laser ablation of sintered film [Fig. 4(b)] predictably showed elevated rim profile due to melt expulsion while laser ablation of unsintered nanoparticle film [Fig. 4(a)] yielded clean features. Figure 4(c) shows submicron lines [full width at half maximum (FWHM): 400–800 nm] with 3 μm pitch. The conductor lines were sintered after ablation and found highly electrically conductive and isolated from each other. Note that the ink-jet printing resolution is 50–100 μm, while such small features would require a photolithographic process. The size of the conductive positive features can be reduced significantly by utilizing higher magnification focusing lens. Even sub-100-μm features will be possible with near field scanning optical microscope-based ablation scheme.

To summarize, by ablating unsintered nanoparticle films, clean and precise patterning characterized by low ablation threshold could be obtained. This could be explained by considering the combined effects of melting temperature depression, lower conductive heat transfer loss, strong absorption of the incident laser beam, and relatively weak bonding between nanoparticles during laser irradiation. The possibility of utilizing high frequency nanosecond laser and a fast x-y galvanometer system could make this method attractive in flexible electronics manufacturing.

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