International Journal of Extreme Manufacturing

PAPER • OPEN ACCESS

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To cite this article: Yoshiki Nakata *et al* 2020 *Int. J. Extrem. Manuf.* **2** 025101

OPEN ACCESS
IOP Publishing | IMMT
International Journal of Extreme Manufacturing
Int. J. Extrem. Manuf. **2** (2020) 025101 (5pp)
https://doi.org/10.1088/2631-7990/ab88bf

Nanodot array deposition via single shot laser interference pattern using laser-induced forward transfer

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Received 20 January 2020, revised 26 March 2020
Accepted for publication 13 April 2020
Published 14 May 2020

Abstract

Laser-induced forward transfer (LIFT) is a direct-writing technique capable of depositing a single dot smaller than the laser wavelength at small shot energy through the laser-induced dot transfer (LIDT) technique. To deposit a single nanodot in a single shot of laser irradiation, a liquid nanodrop is transferred from donor to receiver and finally solidified via a solid–liquid–solid (SLS) process. In conventional LIDT experiments, multi-shots with step scanning have been used to form array structures. However, interference laser processing can achieve an arrayed process and generate a periodic structure in a single shot. In this study, a femtosecond laser interference pattern was first applied to LIDT, and an array of nanodots was successfully deposited in a single shot, producing the following unit structures: a single dot, adjoining dots, and stacking dots. The diameter of the smallest nanodot was 355 nm, and the narrowest gap between two adjoining nanodots was 17.2 nm. The LIDT technique produces high-purity, catalyst-free that do not require post-cleaning or alignment processes. Given these significant advantages, LIDT can expand the usability of nanodots in a wide range of fields.

Keywords: interference laser processing, laser-induced dot transfer, nanodot, array, femtosecond laser, solid–liquid–solid mechanism, Au

(Some figures may appear in colour only in the online journal)

1. Introduction

Laser-induced transferring techniques have been investigated since the 1970s. The first trial of laser-induced forward transfer (LIFT) was called material transfer recording and used a typewriter ribbon as a source material [1]. The ink was irradiated in either forward or reverse directions and transferred onto a receiver substrate facing the target in or out of contact, as shown in figure 1. Target materials later expanded to include thin metal films [2, 3], oxides [4, 5], fluorescent materials [6], and biomaterials [7]. The mechanisms underlying LIFT have been verified by the finite element method [5] and studied by particle type dependent imaging methods [3, 8, 9]. Laser-induced dot transfer (LIDT) is a technique that utilizes relatively small shot energies to deposit droplets smaller than the laser wavelength on a receiver [10–13]. Nanodroplets, or nanodots, can also be deposited on a source target and collected—this

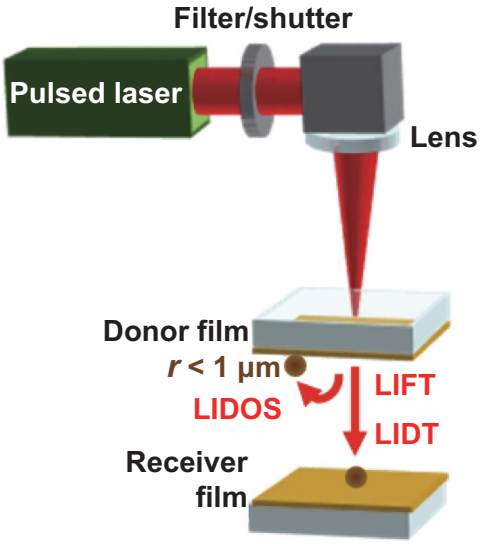

Figure 1. Schematic illustration of a LIFT, LIDT, and LIDOS process.

technique is called laser-induced dot caught on source target (LIDOS) [14].

Metal nanoarray structures have been applied to optical and plasmonic devices such as computer-generated holography [13], chromatism [15, 16], transmittance control [17], and plasmonic scattering structure [18]. The periodicity of the nanostructures is the key to determining their properties and functions. A conventional LIFT or LIDT process with step scanning can fabricate such devices, but this multi-step process is time-consuming and the precision of the period depends upon the accuracy of the translation stage or Galvano scanner.

Interference laser processing produces multiple spots in a lattice in a single shot of laser irradiation, and periodic nanostructures in a lattice, such as nanobit, nanobump [19], nanodrop [19–21], nanocrown [22], nanowhisker [23], and nanoholes [19, 24, 25]. In this work, the interference laser processing technique was first applied to LIDT, and a nanodot array was deposited in a single shot. The resultant structures were investigated by optical microscope and scanning electron microscope (SEM).

2. Experimental setup

The experimental setup is shown in figure 2. An fs laser with a 785 nm wavelength and a 240 fs pulse width was used. The pointing of the fs laser fluctuated by mrad h^{-1} order, so it was stabilized with a piezo-actuator controlled mirror and pointing monitor feedback system by <10 μrad h^{-1} (ASM003, PDP90A and special order system, Thorlabs, Inc.). The beam was split by a diffractive optical element (DOE: HOLO/OR Ltd, special order) into four 1st order diffracted beams and aimed at a thin Au donor film ($t = 40$ nm) through a transparent substrate via a de-magnification system consisting of two convex lenses ($f_1 = 200$ nm, $f_2 = 50$ nm). The zero-order beam was discarded. The period of the interference pattern, which can be controlled by the diffraction angle and the demagnification factor, was $\Lambda = 3.6\,\mu$m. A thin Au receiver film was placed in contact facing the donor film ($t = 100$ nm). The LIDT experiment was performed in a vacuum chamber ($P < 1.3$ kPa).

3. Experimental results

3.1. Array of Au nanodots

Figure 3 contains (a) optical and (b) SEM images of the same Au nanodot array deposited by LIDT with an interference pattern. The shot energy was 97 μJ, and the averaged fluence ($1/e^2$) was 133 mJ cm^{-2}. The picture was taken to cover the area with the highest concentration of deposited nanodots. It is apparent that nanodots were successfully deposited in an array in a single shot of laser irradiation. 191 nanodots were fabricated on a 12 × 17 matrix at a deposition efficiency rate of 94%.

Figure 4 provides a schematic explaining the underlying mechanical processes of LIDT using an interference pattern. First, laser energy is induced into the donor film periodically according to the interference pattern, as shown in the top inset. Next, the resulting thermal expansion and vapor pressure creates a nano- sized area of melted metal in a spot in the interference pattern, as represented in figure 4(b). Then, a nanodot is formed due to surface tension, as shown in figure 4(c). In the case of laser processing without a receiver, a nanodrop [19, 21, 23] or nanowhisker [23] forms through a solid–liquid–solid (SLS) mechanism [23, 26] instead of a vapor-liquid-solid (VLS) mechanism [27]. In the case of LIDT, the nanodot detaches from the summit of the nanowhisker and adheres to the receiver film facing the donor film. The nanodot is deposited as the temperature decreases due to thermal diffusion, as shown in figure 4(d). Unlike single LIDT using a focused laser spot, neighboring spots in a matrix with $\Lambda = 3.6\,\mu$m distance are irradiated simultaneously. It should be noted that the LIDT process starts before the temperature along the horizontal plane of the donor film stabilizes.

There are some missing and surplus depositions, as shown in figure 3. The former would be due to failure in ejection or deposition, and the latter would be due to dislocation in or after the process or multiple ejections, as explained in the next subsection.

3.2. Single, adjoining and stacking Au nanodots

In LIDT, the number of nanodrops in a single shot depends on the parameters. Dr. Narazaki reported that the number of deposited $FeSi_2$ nanodots increases as a function of fluence [10]. On the other hand, single and multiple nanodots were deposited at different spots in this experiment. In the SEM observation, a structure with multiple nanodots was seen at the center, where the fluence was relatively high. A flattop beam can produce nanodots of uniform size and number [28].

Figures 5(a-1) and (a-2) contain top and bird's eye view images of solo nanodots in the array shown in figure 3. Each red arrow indicates the direction of the observation in the bird's eye view. The shape is a squashed sphere, which indicates that

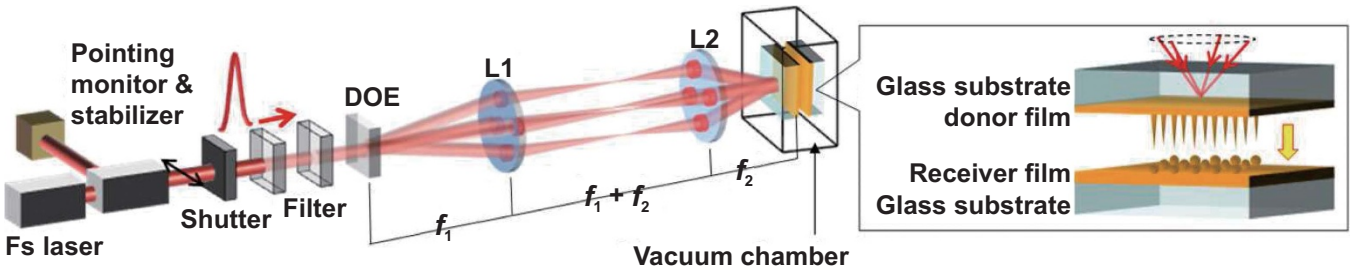

Figure 2. Experimental setup of LIDT with an interference pattern.

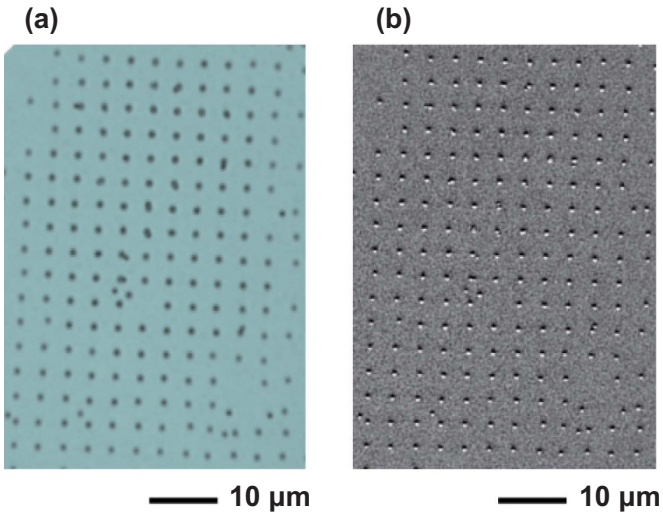

Figure 3. Au nanodot array deposited by LIDT with interference pattern. (a) Optical image and (b) SEM image.

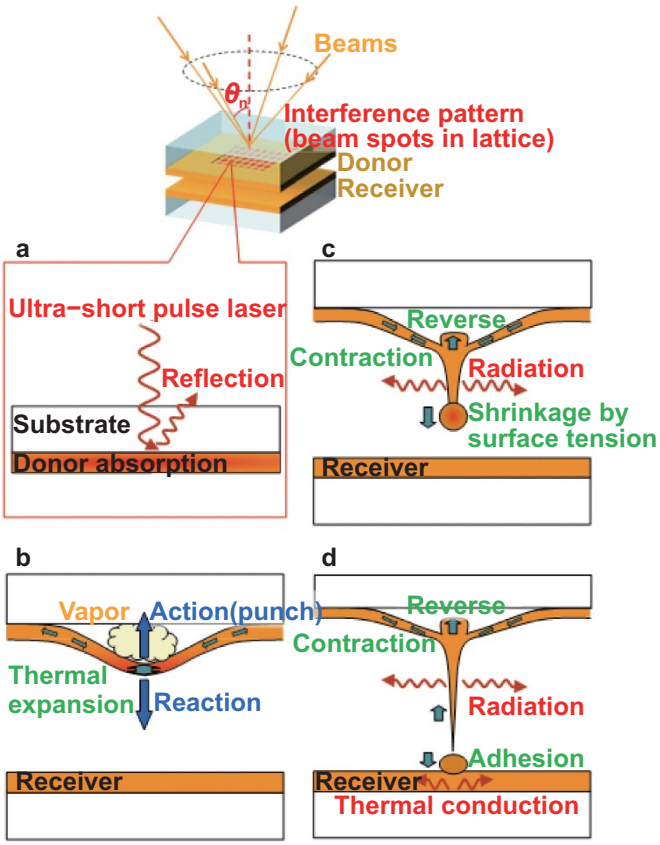

Figure 4. A schematic explanation of LIDT using an interference pattern. Top inset explains the scheme. (a) Induction of laser energy into a spot in an interference pattern on the donor film. (b) Launch of a solute metal film by thermal expansion and vapor pressure. (c) Formation of a nanodot on the summit due to the shrinkage caused by surface tension. (d) Adhesion of the nanodot to the receiver film.

the nanodot was soft and the temperature was high enough at the time of adhesion. The diameter is 538 nm and 484 nm, respectively. The nanodot and nanowhisker formed simultaneously, as shown in figure 4(d), which corresponds with observations from paper research on nanowhisker formation [23]. Similarly, paired nanodots were deposited in a single shot, as shown in figures 5(b-1) and (b-2) in adjoining configuration and in figures 5(c-1) and (c-2) in stacking configuration. The deposition of paired nanodots in a spot means that they are supposed to be ejected from the same spot in an interference pattern. Consecutive formation of nanodots from a single spot may occur when the melted film exists for an extended period. Multiple ejections and depositions were observed in both single spot LIDT [10, 29] and LIDOS [14]. The mechanism of multiple formation may be Rayleigh-instability, which has been observed by time-resolved imaging of liquid behavior [30–32]. Considering the deposition sequence in figures 5(c-1) and (c-2), the subsequent ejection produced a smaller nanodot. The average diameter of the larger base and smaller top nanodots are 592 nm and 389 nm, respectively. The smallest nanodot was 355 nm, as shown in figure 5(c-1).

The horizontal spacing between nanodots in the case of multiple ejections depends on the direction of each ejection. It is suspected that the direction fluctuates, forming either adjoining or stacking structures. The gap in figures 5(b-1) and (b-2) measure 81.9 nm and 17.2 nm, respectively. A nanogap structure elicits a field enhancement effect, which will be useful for plasmonic applications, such as surface-enhanced Raman scattering.

We compared LIDT with other techniques, including LIDOS, which can also be used to fabricate nanodots [14]. In this technique, nanodots deposit on the source film, as shown in figure 1. The experimental setup was nearly identical to the LIDT setup, except the receiver substrate was excluded. The difference on the side of the deposition would be due to parameters, such as atmospheric conditions,

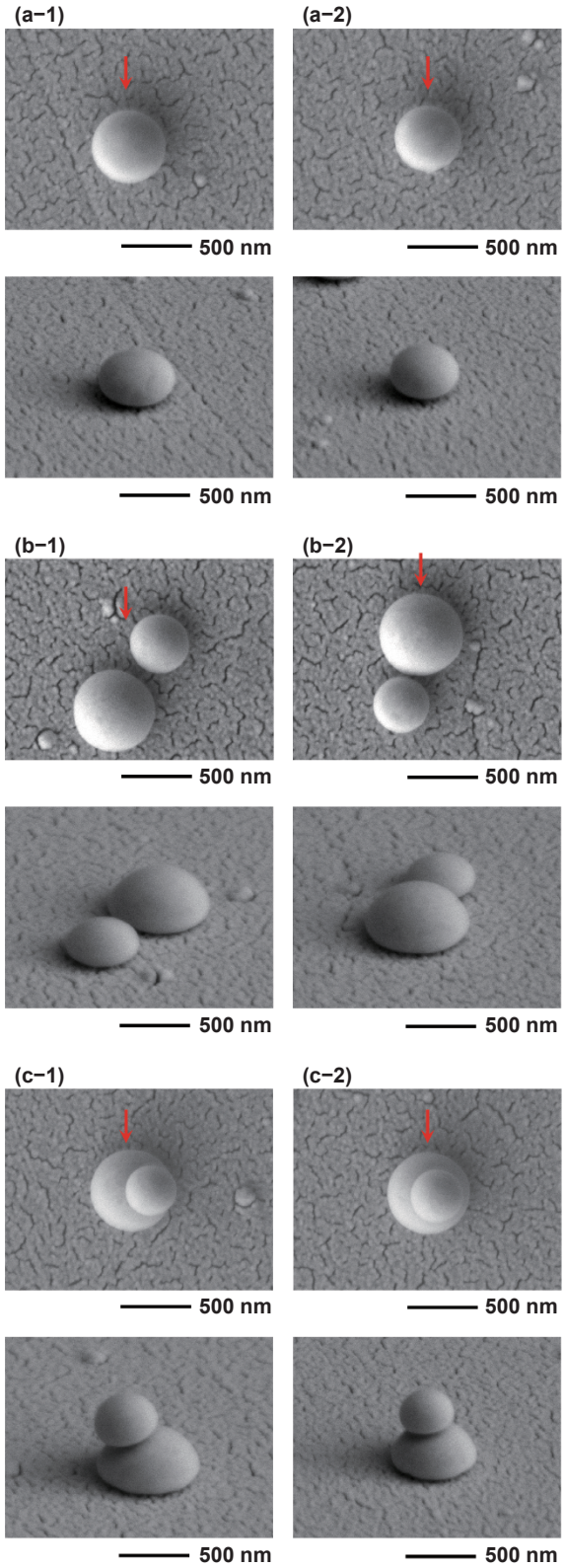

Figure 5. SEM images of (a-1), (a-2) single nanodot, (b-1), (b-2) adjoining nanodots, and (c-1), (c-2) stacking nanodots.

film thickness, fluence, etc. LIDOS experiments took place in atmospheric room-temperature conditions, while LIDT experiments occurred in a vacuum. It is possible that air cerates drag on the ejected particle as it returns to the donor film, in the case of LIDOS. The LIDOS-fabricated nanodots had an average diameter of 376 nm the film thickness was 40 nm, which is similar to the one used this experiment. The pulsed-laser deposition technique can eject multiple droplets from the ablation spot in a single shot, but the size is dispersed [33]. Lithographic techniques can fabricate nano-sized structures, but these techniques are time consuming and expensive [34]. Chemosynthesis methods lack size uniformity and require post processing steps, such as alignment and cleaning. LIDT using an interference pattern has many advantages compared to conventional techniques.

Based on two-dimensional laser-induced fluorescence (2D-LIF) observations from our previous work on single spot LIFT of thin Au film, we concluded that the presence of air significantly limits the velocity and divergence angle of the ejected atoms and particles [3, 35]. LIFT of dye film led to minimal atmospheric deposition [6]. The atmospheric condition may also affect LIDT using interference patterns. For example, the LIDOS experiments, mentioned above, resulted in successful nanodot deposition in atmospheric room-temperature conditions.

4. Summary

An interference pattern was first applied to the LIDT process, and Au nanodot array was successfully deposited in a single shot. The unit structure was single, adjoining or stacking nanodots. The smallest nanodot diameter was 355 nm, which is on the same order as LIDOS.

LIDT offers serval advantages, including high adaptability to different materials, reduced time and cost consumption, and high purity. In addition, a multi-shot process using different targets enables the fabrication of a heterostructure. However, LIDT with interference patterns does not require any alignment processes, making it a more advantageous and less time alternative to conventional multi-shot techniques. As explained in the previous subsection, uniformity of size and shape is possible by using a flattop beam. These advantages will expand the application fields of nanodot array in photonics, plasmonics and nanotechnology.

Acknowledgments

This research was financially supported by the Japan Society for the Promotion of Science (JSPS) through a Grant-in-Aid for Scientific Research (B) (No. 16H038850) and Amada Foundation for Metal Work Technology (AF-2018212).

Author contributions

Y N planned and organized the project. He also performed all experiments and analyses. K T supported the beam pointing stabilizer system. E H partly helped the beam alignment. Y N wrote all text and prepared all figures. N M partly supported the experimental environment. Y N, N M, A N, T S, and Y T supported the application of JSPS financial support program.

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