Continuous Nanoparticle Assembly by a Modulated Photo-Induced Microbubble for Fabrication of Micrometric Conductive Patterns

Nina Armon,1 Ehud Greenberg,1 Michael Layani,2 Yitzchak S. Rosen,2 Shlomo Magdassi2,3 and Hagay Shpaisman1∗

1 Department of Chemistry and Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat Gan 5290002, Israel
2 Casali Center for Applied Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
3 School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

* hagay.shpaisman@biu.ac.il

Abstract

The laser-induced microbubble technique (LIMBT) has recently been developed for micro-patterning of various materials. In this method, a laser beam is focused on a dispersion of nanoparticles leading to the formation of a microbubble due to laser heating. Convection currents around the microbubble carry nanoparticles so that they become pinned to the bubble/substrate interface. The major limitation of this technique is that, for most materials, a non-continuous deposition is formed.
We show that continuous patterns can be formed by preventing the microbubble from being pinned to the deposited material. This is done by modulating the laser so that the construction and destruction of the microbubble is controlled. When the method is applied to a dispersion of Ag nanoparticles, continuous electrically conductive lines are formed. Furthermore, the line width is narrower than that achieved by standard non-modulated LIMBT. This approach can be applied to the direct-write fabrication of micron-size conductive patterns in electronic devices, without the use of photolithography.

Keywords: Directed assembly, Microbubble, Pinning, Pattern formation, Direct laser writing, Nanoparticle assembly


**Introduction**

Various direct writing techniques are used to form patterns and micro-structures for many purposes in electronics, sensing, medicine and human healthcare applications.\textsuperscript{1} These techniques can be divided into two main categories: top-down and bottom-up. Top-down methods generally suffer from a waste of material. Many of the methods that use this approach are based on lithography.\textsuperscript{1-5} However, these methods have several disadvantages such as the need for a photoresist and pattern masks which limits their use.

The bottom-up approach includes many techniques such as inkjet printing,\textsuperscript{6} atomic-layer deposition,\textsuperscript{7} sol-gel nanofabrication,\textsuperscript{8} molecular self-assembly\textsuperscript{9} and laser chemical vapor deposition.\textsuperscript{10} A newly developed technique based on the pinning of particles to the bottom of a microbubble,\textsuperscript{11} formed by laser heating, forms the focus of this paper. This technique is referred to as laser-induced microbubbles,\textsuperscript{12,13} thermo-optically manipulated laser induced microbubbles,\textsuperscript{14} optothermally generated bubbles,\textsuperscript{15} continuous-wave laser-induced vapor bubbles,\textsuperscript{11} laser-induced micronanobubbles,\textsuperscript{16} micronanobubbles formed by local laser heating\textsuperscript{17}, bubble printing\textsuperscript{18,19} and bubble-pen lithography.\textsuperscript{20} For simplicity and clarity, we will systematically use the term laser-induced microbubble technique (LIMBT).

In LIMBT, a laser beam is focused on a dispersion of nanoparticles (NPs). As the particles absorb the light and their temperature rises, the vapor pressure of the surrounding medium increases until, eventually, a microbubble is formed. Then, two types of convective flow occur: natural and Gibbs–Marangoni convection. Natural convection arises from density differences due to a temperature gradient between the top and bottom of the microbubble. As the hotter medium has lower density, it flows upwards. The Gibbs–Marangoni convection results from a surface-
tension gradient within the dispersion in the vicinity of the microbubble. As the bottom of the microbubble has a lower surface tension than its upper part, the dispersion flows to the upper part of the microbubble. To compensate for these convections that stream the dispersion upwards, there is also flow toward the bottom of the microbubble. If the focal point is near the substrate, particles carried by the dispersion will be pinned to the bubble/substrate contact area (Figure 1). Moving the focused beam relative to the sample results in the migration of the microbubble and the deposition of fresh material at the bubble/substrate contact area.

![Figure 1. Illustration of the LIMBT mechanism. Convective flows (originating from the temperature and surface-tension gradients between the upper and lower parts of the microbubble) carry NPs to the bubble/substrate interface, where they are pinned.](image)

In previous studies, various materials such as glycine,12,14 CdSe/ZnS Q dots,16 CdSe/CdS Q dots,18,19 DNA,17 soft oxametalates,14,21 carbon nanotubes,14 ZnO13 and polysterene11,14 were manipulated using LIMBT. In some studies,14,21,22 the manipulated particles absorb the laser light
to activate LIMBT. In others, where the particles cannot absorb laser light, the substrate is covered by a metallic layer to promote light absorption.11–13,15–20,23 Researchers have systematically studied the influence of the size of the objects, nanoparticles versus agglomerates,22 and the thickness of the metallic film23 on material deposition. Others have theoretically analyzed12,15,20,22 and computationally simulated15,20 LIMBT.

The use of substrates coated by metals or indium tin oxide13 has several benefits such as the ability to direct any desired material, even if the material does not absorb laser light. Another advantage is that relatively low laser powers can be used for bubble generation, as the plasmon resonance of the metal can be matched to the wavelength of the laser,20 leading to sub-micrometer patterns.19 However, the metallic coating also has several disadvantages, such as adding another stage to the sample preparation which is time consuming and increases the cost of each sample. Additionally, as the entire substrate is conducting, this method may not be suitable for various micro-electronic applications where conductance is only required for the patterned NPs. Here, we focus on pattern formation on non-coated glass substrates.

Currently, LIMBT has two main limitations: inconsistent continuity and a minimum linewidth of ~4 µm14 for cases without any metal coating on the substrate. So far, continuous patterns have only been reported for soft oxometalates,14,21 while most studies show images that demonstrate non-continuous patterns11 or do not address this issue at all. In this work, we describe the reasons for the current limitations of uncontrolled micro-bubble growth and pinning, and show how modulation of the laser enables the formation of thin continuous patterns due to improved control over the microbubbles.
Results and Discussion

As a model system, we used Ag NPs that were synthesized as described by Magdassi et al.,\textsuperscript{24} yielding nanoparticles which are stabilized by polyacrylic acid sodium salt. Dispersions with various concentrations of nanoparticles in diethylene glycol butyl ether (DB) were used in this study. For all the experiments, we used 2 wt% dispersions unless stated otherwise.

A 532 nm laser was focused on the dispersion which was inserted between two glass slides. The microscope stage was computer-controlled and the experiments were recorded using a camera. The optical setup is illustrated in Figure 2. To form patterns, the microscope stage was moved along a predetermined path by computer software and the stage velocity was set to 10 \( \mu \text{m/s} \), unless stated otherwise.

![Figure 2. Illustration of the optical setup. A laser beam is relayed to the objective lens by a dichroic mirror. The inset illustrates the pattern formation by NPs that are deposited by following the focal point.](image)
Writing experiments that were conducted at various NPs concentrations (0.5–10 wt%), varying both laser powers (1–140 mW) and stage velocities (10 µm/s – 9 mm/s), did not lead to the formation of continuous lines. **Figure 3a** demonstrates such a typical non-continuous line formed by 25mW laser power.

![Image of Experiment](image)

**Figure 3.** Bright-field microscopy images of (a) non-modulated LIMBT leading to non-continuous material deposition and (b) modulated LIMBT resulting in a continuous line.

The reason for the discontinuity of line formation which is one of the current limitations of LIMBT is that the formed microbubble advances in a non-continuous manner. This is evident from **Figure 4** and Video S1 in the Supplementary Information. The advancing stage moves the laser focal spot, but the microbubble fails to follow, as it is pinned by the materials that are being deposited at the microbubble base (**Figure 4b, 25mW**). The red dashed lines show the microbubble edges and illustrate how the microbubble, and the deposited material, is shifted off-center from the laser focal spot, compared to the initial state at **Figure 4a,** due to pinning. The microbubble, eventually, leaps forward to be centered at the focal spot (**Figure 4c**), but this leap results in non-
continuous material deposition. The pinning of the microbubble is more noticeable for water dispersions (see Figure S1a and Video S2 in the Supporting Information section).

![Figure 4. Bright-field microscopy images of the microbubble without modulation. The red dashed lines show the microbubble edges. (a) At t=0 sec, the microbubble and the deposited material are centered at the laser focal spot (bright green). (b) At t=0.5 sec, the microbubble is shifted off-center from the laser focal spot as it is pinned to the deposited material. (c) At t=1 sec, the microbubble is again centered at the focal spot.

We thus aimed at ensuring that the microbubble advances in an undisturbed manner so that continuous deposition is achieved. We found that by modulating the laser beam to control the formation and destruction of the microbubble, continuous material deposition can be achieved (see Video S3 and Video S4 for DB and water dispersions, respectively). Modulation of the laser is
performed by a mechanical shutter, an optical chopper or by controlling the power delivered to the laser diode. We found that all the methods give similar results for the same parameters, but each instrument has a limited range of parameters.

**Figure 3b** shows that using a modulated laser (140mW, with 1 kHz modulation at 20% duty cycle, unless stated otherwise) results in continuous deposition; see also **Figure S1b** for similar results for aqueous dispersion. When the laser is turned on, its energy is transferred to the microbubble, resulting in its expansion\(^{14,25}\) and material deposition.\(^{22,23}\) Once the laser is turned off, the microbubble rapidly collapses.\(^{14}\) We hypothesize that if the microbubble totally collapses, a new microbubble is formed at a new location, determined by the stage movement, when the laser is turned on again. Depending on the modulation parameters of higher frequencies and duty cycles, the microbubble may shrink rather than totally collapse. In this case, the microbubble edges are detached from the deposited material and, once the laser is turned on, the microbubble follows the focus of the laser due to Marangoni convection flow.\(^{14}\) Either way, the pinning of the microbubble is avoided and better control over its size is achieved. **Figure 5a** shows a complex pattern ("BIU", Bar-Ilan University) formed by the stage movement. **Figure 5b** shows a cross-section of the continuous line formed by modulated LIMBT that shows the close packing of the deposited Ag NPs. The cross-section was produced using a focused-ion beam (FIB). We have also demonstrated
how modulated LIMBT allows continuous line formation of other NPs such as copper formate NPs\textsuperscript{26} as a precursor for copper, see Supporting Information.

![Figure 5](image)

**Figure 5.** (a) A complex pattern ("BIU", Bar-Ilan University) formed by modulated LIMBT. (b) Cross-section (by FIB) of the lines produced by modulated LIMBT. (c) SEM image of a thin Ag line.

To confirm the continuity of the Ag lines, they were imaged by SEM, and their conductivities were measured. **Figure 6a** shows a SEM image of a line, without any further treatment, that seems to be robust and continuous. In order to obtain electrical conductivity, nanoparticle-based inks require an additional post-deposition step of sintering. We have thus performed three types of sintering: laser sintering, thermal sintering and room-temperature chemical sintering\textsuperscript{24,27} Room-temperature sintering was achieved by exposing the formed lines to vapors of HCl solution (32\%) for 30 seconds (**Figure 6b**). The HCl vapor causes a decrease in NP stabilization followed by the detachment of the anchoring groups from the NP surface,\textsuperscript{27} resulting in nanoparticle sintering. **Figure 6c** shows a SEM image of the lines after laser sintering. Laser sintering is performed on the sample after removal of the Ag dispersion followed by drying with a nitrogen spray gun. The modulated laser is focused on the lines and locally heats them resulting in sintering. **Figure 6d** shows the deposited Ag NPs after oven heating at 300 °C for 30 minutes. Laser- and room-temperature sintering produce NPs that are somewhat better merged compared to the untreated
sample. However, the best merging of the NPs is obtained using oven sintering. This is in agreement with the better conductivity values which derive from electrical percolation between the particles, despite the pores.

Figure 6. SEM images of Ag NPs after line formation with a modulated LIMBT. (a) Untreated sample, followed by the same samples after 3 different sintering procedures: (b) exposure to HCl vapors, (c) laser sintering and (d) sintering with oven at 300 °C. The inset in (c) is a typical line demonstrating the continuity of the formed lines by LIMBT.

The highest conductivity values that we have measured reveal that, indeed, these patterns are continuous over 2 mm, as seen in Figure S2, with a resistivity of $3.9 \times 10^{-6} \pm 1.7 \times 10^{-6} \ \Omega \text{m}$ (width: $14.24 \pm 1.08 \ \mu m$, height: $599 \pm 71 \ \text{nm}$) before sintering. In general, it was found that the resistivity of the lines decreases after applying each of the three types of sintering presented above. After sintering with HCl, the resistivity was $9.8 \times 10^{-7} \pm 1.6 \times 10^{-7} \ \Omega \text{m}$, after laser sintering it was $1.13 \times 10^{-6} \pm 4.4 \times 10^{-7} \ \Omega \text{m}$ and after oven sintering it was $4.92 \times 10^{-7} \pm 1.4 \times 10^{-7} \ \Omega \text{m}$. For comparison, the resistivity of bulk silver and the sintered inkjet printed Ag NPs$^{28}$ used in our experiments is $1.59 \times$
$10^8 \, \Omega \text{m}$ and $5.9 \times 10^8 \, \Omega \text{m}$, respectively. **Figure 7** shows typical I-V curves for bare Ag lines and after the various post-treatments.

![I-V curves for Ag NPs deposited as lines before and after sintering with HCl vapor, oven and laser.](image)

**Figure 7.** Typical I-V curves for Ag NPs deposited as lines before and after sintering with HCl vapor, oven and laser.

Each of these three sintering methods has its own advantages and disadvantages. Oven sintering is very simple but requires high temperatures that often limit the materials that can be used. The chloride-ion treatment has the advantage of being performed at room temperature but the acid may have a negative impact on adjacent materials/devices. Laser sintering does not require any additional equipment as it uses the same laser as for material deposition and can be applied locally (for controlled resistance), but may be more time-consuming for large and complex samples.
Modulated laser light also enables simple control of the width and height of the lines. The effect of the frequency and duty cycle on the average width of the patterns (determined by image analysis from bright-field microscopy) is shown in Figures 8a and 8b, respectively. To achieve minimal line width (see below), we used a 0.5 wt% dispersion of Ag NPs with a stage velocity of 30 µm/s, and a 32-mW laser intensity. The duty cycle is fixed at 20% for Figure 8a while, in Figure 8b, the frequency is set to 10 kHz. Each data point was averaged over three separate experiments, measured at 2–5 different locations (all the measured data points are plotted in Figure S3).

![Figure 8](image.png)

*Figure 8. Width of lines as a function of laser frequency (a) and duty cycle (b). The inset in (a) shows a zoom-in of the 0.1-10 kHz data points.*

It is evident from these figures that a narrower linewidth is achieved by using either higher frequencies or smaller duty cycles. We attribute these findings to the maximum size that the microbubble reaches before it collapses due to laser modulation. Smaller duty cycles result in less energy entering the system, causing the formation of a relatively smaller microbubble and thinner deposition. Likewise, at higher frequencies, the microbubble has less time to grow before entering the “off” state and possibly a shorter time for warming, leading to weaker convective flows that results in a thinner deposition. The minimal line width (1.7 µm) was achieved using 10 kHz and
20% duty cycle. This is less than half of the 4 µm line width achieved by state-of-the-art non-modulated LIMBT experiments without surface coating, it therefore overcomes one of the limitations of non-modulated LIMBT.

It should be emphasized that reducing the laser intensity without modulation also results in a decrease in width (see Figure S4 in Supporting Information). However, these lines are not continuous and have a minimum width of 2.5 µm whereas, using modulation, the minimum width is reduced to 1.7 µm. Moreover, we have succeeded in performing deposition of material using modulation at very low intensities where no deposition occurs in its absence (the dispersion used was 0.5 wt% Ag NPs, the laser intensity was set to 3 mW, the duty cycle was 20% and the frequency was 10 kHz).

The effect of the dispersion concentration on the width and height of the lines is shown in Figure 9. The modulated LIMBT is applied on Ag NPs dispersed with 0.5–10 wt%. Deposition with lower concentrations than 0.5 wt% was found to be very sensitive to minute changes in the parameters and is therefore outside the scope of this manuscript. Each data point was averaged over three separate experiments, each producing 3–5 lines that were measured at 2–5 different locations, resulting in at least 40 measurements per data point.
A higher concentration of Ag NPs means that more material is available for deposition. Indeed, with an increase in concentration, there is an increase in both the maximum height and the width of each line. It is noteworthy that the effect on the height is significantly greater than on the width. **Figure 5c** shows a scanning electron microscope (SEM) image of a thin line formed by 0.5 wt% dispersion of Ag NPs. While changing the concentration from 0.5% to 10% results in a three-fold increase in width from 7.6 to 25.64 µm, the increase in height is more than eleven-fold from 213.8 to 2550.33 nm. As NPs are pinned to the bubble/surface interface, the microbubble rises above the deposited material and, therefore, contributes to the material deposition in the vertical direction.

Figure 9. Height (left y-axis) and width (right y-axis) of lines as a function of the dispersion concentration.
Certain combinations of modulations and stage velocities form patterns of rings with controlled spacing, as shown in Figure 10a and Video S5. The grid was produced with Ag NPs while the stage velocity was set to 10 µm/s, the frequency to 1 kHz and the duty cycle to 30%. The mechanical shutter was set to open every 0.1 s and then close for 0.8 s. The reason for the ring formation is that the spherical microbubble promotes material deposition along its contact area with the substrate. The distance (d) between rings can be described as \( \frac{v}{f} \), where v is the stage velocity and f is the frequency, defined as the lowest frequency between the mechanical and electrical modulation. For the conditions stated above, the frequency is 1.11 Hz as the shutter frequency is lower than the frequency of the function generator (1 kHz), leading to d = 9.01 µm.

Figure 10. (a) SEM image showing patterns that are made of rings with controlled spacing. The inset is a magnified image of the grid. (b) Cross-section (FIB) of a ring (from the 8.6 µm ring spacing line). (c) I-V curves of 3 lines, shown in (d), with different ring spacing (5.0, 8.6 and 9.0 µm).
Figure 10b shows the cross-section (achieved by FIB) of a deposited ring where the distance between ring centers is of 8.6 µm. The shape of the cross-section is consistent with the proposed deposition mechanism illustrated in Figure 1. Lines consisting of rings were found to be conductive, as shown in the I-V curves at Figure 10c. Their conductivity is inversely proportional to the distance between the ring centers (Figure 10d). The resistivity of the line with ring spacing of 8.6 µm was 4.4×10⁻⁶ ± 1.1×10⁻⁶ Ωm, similar to the resistivity of full lines before sintering. The cross-section was estimated from Figure 10b to be that of two 2 µm × 1.5 µm rods for each side of the ring.

We have also accomplished writing with stage velocities as high as 9 mm/s which is the upper speed limit of our stage, forming 30 mm long lines (as seen in Video S6). This velocity is similar to the highest velocities currently reported for non-modulated LIMBT (10 mm/s¹⁹ and 1 mm/s¹⁴). After oven sintering the resistivity was 3.16×10⁻⁷ ± 1.01×10⁻⁷ Ωm (width: 18.60 ± 3.05 µm, height: 545 ± 116 nm), similar to the resistivity of lines produced with our standard velocity of 10 µm/s after the same post-treatment. Without oven sintering the fast-printed lines are not conductive, as apparently at this speed the laser does not heat the deposited material enough to allow sintering. Figure 11 shows that even for high stage velocities (9 mm/s), noticeable ring formation can be avoided by increasing the modulation frequency. When the calculated distance between centers of rings is ~1.3 µm or lower (Figure 11f), the separate rings are indistinguishable.
Conclusion

In conclusion, we have demonstrated the micro-patterning of conductive lines and have shown how modulation of the laser significantly improves material deposition using LIMBT. The modulation controls the construction and destruction of the microbubble, thereby preventing pinning of the microbubble to the deposited material and allowing the formation of continuous patterns. We verified the continuity of the lines by conductivity measurements, and showed that the conductivity can be further improved by sintering via chloride ions or heating.

Figure 11. Bright-field optical images (a)-(g) for high stage velocities (9 mm/s) with varying modulation frequencies (1-7 kHz).
We also examined how the modulation parameters of frequency and duty cycle affect the width of the formed patterns, leading to improvement in the minimal width compared to the non-modulated LIMBT for non-coated substrates. We found that the dispersion concentration affects the height of the lines more than their width. Lines made of rings were also demonstrated for specific combinations of modulation and stage velocities. Such rings can be utilized for the fabrication of transparent conductors, which have great importance in optoelectronic devices. Overall, the improved LIMBT can be applied to produce thin conductive patterns for electronic devices and sensor formation.

**Experimental section**

**Sample preparation**

Ag NPs were synthesized as described by Magdassi et al.,\textsuperscript{24} yielding nanoparticles which are stabilized by polyacrylic acid sodium salt (Mw 8000 kD) and have an average size of 50 ± 3 nm and a typical zeta potential of 40 mV. Dispersions with various concentrations (0.5–10 wt%) of nanoparticles in diethylene glycol butyl ether (DB) and water were used in this study.

The preparation of a sample consists of cleaning glass slides (0.17 mm thick) with ethanol, followed by thorough drying. Stretched Parafilm\textsuperscript{TM} is placed between two slides as a spacer. The NP dispersion is inserted between the two slides by capillary forces.

**Optical setup**

The laser system consists of an inverted microscope (Nikon, Eclipse Ti-U) attached to a cw laser system (532 nm CW DPSS laser, 5-532-DPSS-0.5-LN, Altechna). The experiments were performed using a 40X objective lens (0.6 NA, Nikon). The maximal laser power without modulation was 140 mW. All reported laser powers were measured after the objective lens with a
power meter (PM100, Thorlabs) and without applying the modulation. The maximum laser power without modulation was measured also at the back aperture and found to be 170 mW. For our standard conditions (140 mW, 20% duty cycle, 1 kHz) the power at the surface was estimated to be ~3.8 mW/µm². The microscope stage was computer-controlled and the experiments were recorded using a CMOS camera (DPCAM 6CHDMI, DeltaPix). The optical setup is illustrated in Figure 2. The deposition was performed on the bottom slide, as the optical path is minimal (does not pass through the entire liquid phase) and is not distorted by the microbubble. To form patterns, the microscope stage was moved along a predetermined path by computer software and the stage velocity was set to 10 µm/s, unless stated otherwise.

Modulation of the laser is performed by a mechanical shutter (Thorlabs) or an optical chopper (Thorlabs) or by controlling the power delivered to the laser diode. Electrical modulation is achieved using transistor-transistor-logic (TTL) modulation (part of the laser driver circuit). The square-wave signal for the TTL modulation is generated by a Siglent function generator (SDG 5162). We have found that for the same parameters, all the instruments give similar results, but each instrument has a limited range of parameters. The frequency range of the shutter is 0.1Hz - 25Hz, and is used for ring production. The frequency range of the chopper is 60 Hz - 3 kHz, while that of the TTL modulation is 0.1Hz - 100 kHz.

Characterization methods

For conductivity measurements, 5 nm Cr + 100 nm Au pads were sputtered on a glass substrate with 2-mm spacing, and a modulated LIMBT was used to connect the pads. Resistance measurements were performed at a SUSS MicroTec probe station. SEM images were obtained using a Quanta FEG 250 System. Cross-sections were formed by a focused ion beam (FIB) Helios 600 system instrument. To calculate the resistivity, the height and width of the patterns were
measured by a profilometer (Veeco Dektak 150 system). All the conductivity measurements were averaged over at least nine samples.

**Supporting Information**

Comparison between non-modulated and modulated LIMBT for Ag NPs in water; image of 2 mm long line of Ag NPs deposited for conductivity measurements; effect of the frequency and duty cycle on the width of the patterns with all data points; width of lines as a function of non-modulated laser intensity; continuous and conductive copper line formed by Cu formate NPs. (PDF)

Movies showing the production of lines using non-modulated and modulated LIMBT for DB and water dispersions; movie showing production of a grid made of ring shaped lines; movie showing production of lines using the modulated LIMBT with high stage velocity. (AVI)

**Acknowledgments**

The authors acknowledge the help of Moshe Feldberg for his technical assistance with sputtering and the help of Eitan Edri for his assistance with graphics and FIB. This research was partially supported by the Singapore National Research Foundation under the CREATE program: Nanomaterials for Energy and Energy-Water Nexus.
References


Table of Contents

Non-modulated laser

Modulated laser