

Reusable laser-absorbing layers for LIFT

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ABSTRACT

The use of laser induced forward transfer (LIFT) techniques for printing materials for sensor and electronics applications is growing as additive manufacturing expands into the fabrication of functional structures. LIFT is capable of achieving high speed/throughput, high-resolution patterns of a wide range of materials over many types of substrates for applications in flexible-hybrid electronics. In many LIFT applications, the use of a sacrificial or laser-absorbing donor layer is required despite the fact that it can only be used once. This is because the various types of release layers commonly in use with LIFT are completely vaporized when illuminated with a laser pulse. A better solution would be to employ a reusable laser absorbing layer to which the transferable ink or material is attached and then released by a laser pulse without damage to the absorbing layer, therefore allowing its repeated use in subsequent transfers. In this work, we describe the use of two types of reusable laser-absorbing layers for LIFT. One is based on an elastomeric donor layer made from poly(dimethylsiloxane) or PDMS, while the other is based on a ceramic thin film comprised of indium tin oxide (ITO). These release layers have been used at NRL to transfer a wide range of materials including fluids, nanoinks, nanowires and metal foils of varying size and thickness. We will present examples of both PDMS and ITO as donor layers for LIFT and their reusability for laser printing of distinct materials ranging from fluids to solids.

Keywords: Laser-induced forward transfer (LIFT), reusable laser-absorbing layers, LIFT of metal foils, LIFT of nanowires, Laser direct-write, digital microfabrication

1. INTRODUCTION

Laser-induced forward transfer (LIFT) has enabled the fabrication of 2D, 3D, and conformal microstructures utilizing a wide variety of materials onto a diverse set of substrates. This digital microfabrication technique offers the unique advantages of high speed and throughput with high resolution and placement precision.¹ Microstructures made of high viscosity Ag nanopastes exhibiting high aspect ratios for vertical chip integration^{2,3} and freestanding structures⁴ comprised of solid metal foils⁵ that can span device gaps have been successfully demonstrated. Frequently, the materials forming these structures require a sacrificial layer to absorb the laser energy, vaporize and thus propel the voxels of material to be printed forward onto the receiving substrate. There have been many different materials presented for use as sacrificial donor layers, including titanium⁶, triazene polymers⁷, and indium tin oxide⁸. Because these sacrificial layers absorb the bulk of the laser energy, the device or material to be transferred typically does not suffer any degradation upon transfer. However, it is possible for a small amount of donor layer residue to remain on the surface of the printed material after transfer. Using these sacrificial layers allows for small, fragile microelectronic components to be placed without damage that would otherwise be caused by use of a traditional pick and place machine, which are limited in the device sizes they can handle.⁹ While these approaches offer some unique advantages, they

suffer from the fact that the donor substrate cannot be reused. Once the sacrificial donor layer has been used once, it is no longer viable as the laser absorbing material is decomposed or ablated and removed. A donor layer that could be used to transfer a variety of materials but remain undamaged during the laser transfer process would offer an alternative that could save time and cost because it could be used multiple times while also being environmentally friendly. The use of poly(dimethylsiloxane), or PDMS, as a reusable release layer for both stamping¹⁰ and laser-based printing processes¹¹ has been explored by other research groups. John Rogers' group investigated the use of PDMS for printing of Si chips via a laser-assisted delamination process. Because PDMS is a viscoelastic material, the mechanism relies on the laser energy giving rise to different thermo-mechanical responses between the PDMS and the Si chip, propelling the latter forward onto the receiving substrate.¹² Similar to LIFT of inks and pastes, this process is non-contact and capable of printing various solid materials, including semiconductor devices, without a sacrificial layer.¹³ In addition, we have previously demonstrated the use of PDMS as a reusable release layer for the transfer of solid Cu metal foils, characterizing the positional accuracy as a function of laser fluence and donor-to-receiver-gap distance.¹⁴ In the current work, we use PDMS as a reusable release layer for LIFT of Ag nanoink. The PDMS is patterned with microwells ($\sim 5\text{ }\mu\text{m}$) that are then filled with ink. Because the laser spot ($\sim 125\text{ }\mu\text{m}$) is significantly larger than the Ag microwells, multiple Ag microdrops are transferred at the same time. Because the materials that are being printed are liquids and not solid foils, the physical mechanism for transfer is likely vaporization of solvent due to laser absorption in the ink, causing bubble formation and ultimate ejection onto the receiving substrate. We have determined that LIFT of Ag nanoink is possible without damaging the PDMS patterned release layer, thus making it truly reusable.

In addition to investigating PDMS patterned release layers for LIFT of liquids, we demonstrate the use of thin indium tin oxide (ITO) layers as reusable layers for the laser transfer of metal nanowires onto an interdigitated electrode (IDE) platform. ITO as a donor layer has been studied previously for the transfer of both solid metal foils⁸ and ferroelectric thin films¹⁵, where the ITO is decomposed causing an expansion and rise in pressure propelling the printed material forward. Here, we demonstrate the use of ITO as a photothermal layer that remains undamaged by the laser transfer process. The ITO film absorbs the laser energy causing a rise in temperature, which in turn vaporizes the solvent containing the nanowires. Because the laser energy required to transfer the nanowires remains below the damage threshold of the ITO, the donor layer is reusable. Although the mechanism of laser transfer is different for both of these donor layers (PDMS and ITO), they both show no signs of damage at the laser fluences required for successful material transfer. Thus, the laser transfer of a wide variety of materials, from liquids to solids, using reusable layers becomes possible.

2. EXPERIMENTAL METHODS

2.1 Laser-induced Forward Transfer (LIFT)

All LIFT experiments discussed in this paper were performed using the same experimental set-up. A frequency tripled Nd:YVO₄ (JDSU Q301-HD, $\lambda = 355\text{ nm}$, 65 ns FWHM) was used to print the various structures discussed, including both liquid (Ag nanoink) and solid metal (SnO₂ nanowires). A constant repetition rate of 30 kHz was used to guarantee stable pulse energies in conjunction with an acousto-optic modulator which acts as a pulse picker. Lenses and apertures were used to shape the laser beam to the desired size while a CCD camera was placed in-line with the objective for real-time viewing of the transfer process. A more detailed description of the LIFT process can be found in previously published results.¹⁶ Typical laser fluences required for LIFT using reusable release layers were $\sim 95\text{ mJ/cm}^2$ for Ag nanoink on PDMS and $\sim 270\text{ mJ/cm}^2$

for SnO₂ nanowires on ITO.

2.1.1 Preparation of PDMS patterned release layers

Large area transfers of Ag inks were performed using reusable PDMS patterned release substrates. The PDMS donor substrates consisted of hexagonally packed microwells, with circular diameters of $\sim 5\ \mu\text{m}$. To fabricate these patterned donor layers, PDMS (Dow, Sylgard 184) was poured over a Si master, which was fabricated using standard lithography techniques in conjunction with a cryo RIE etch. Once the PDMS was cured (25°C, 48 hrs), it was removed from the master revealing a donor substrate patterned with microwells. Ag nanoink (Cabot Corp., CCI-300) was drop casted onto the PDMS surface relying on capillary wetting. Due to the surface morphology of both the Ag nanoink and the PDMS, no excess Ag nanoink remained on the surface. Once dosed, the PDMS donor was placed upside down onto the receiving substrate, which consisted of a glass slide coated with a thin layer of PDMS. LIFT was performed using an identical setup as discussed previously. A laser spot of $\sim 125\ \mu\text{m}$ was used to transfer multiple Ag microdrops at once. By stepping and repeating, a full pattern of Ag microdrops was printed. No spacers were used between the donor and receiving substrates. A schematic of the PDMS patterned release layer fabrication process can be seen in Figure 1.



Figure 1. Schematic depicting fabrication of PDMS patterned donor layer and subsequent laser transfer of Ag nanoink onto receiving substrate.

2.1.2 Fabrication of electrodes for laser transfer of nanowires

Typical photolithographic techniques were used to fabricate the IDEs (receiving substrate) for the laser transfer of nanowires. LOR 3A (MicroChem Corp., $\sim 300\ \text{nm}$) and S1805 (MicroChem Corp., $\sim 500\ \text{nm}$) were spin coated onto an oxidized silicon wafer ($\langle 100 \rangle$ single crystal silicon with $300\ \text{nm}$ of thermal oxide) in order to perform a bilayer lift-off process. The LOR layer was baked at 185°C for 5 min, whereas the S1805 was baked at 115°C for 1 min. The photoresist was exposed ($\sim 55\ \text{mJ}/\text{cm}^2$) using a quartz photomask (Photo Sciences, Inc.) in a UV mask aligner (MJB3, Suss MicroTec). After photoresist development, any remaining residue was removed with an oxygen plasma treatment (March Plasma, 50 W for 20 – 60 sec). The metal layers (10 nm Ti / 100 nm Au) were deposited using an electron beam evaporator (FC 1800, Temescal) followed by lift-off. The patterned IDEs had an electrode width and spacing of $2\ \mu\text{m}$.

2.1.3 Preparation of nanowires and ITO donor layers

The SnO₂ nanowires were fabricated using a chemical vapor deposition (CVD) system and then removed from the substrate via sonication in ethylene glycol.¹⁷ The donor substrate consisted of an ITO-coated glass substrate (Delta Technologies Ltd., $50 \times 75 \times 0.5\ \text{mm}$ glass slide with a $200\ \text{nm}$, as measured by stylus profilometry, ITO coating on one side) that was sonicated in isopropanol and treated with an oxygen plasma before use. The nanowire suspension was spin-coated onto the donor substrate, which at this point was ready for immediate use. The donor surface was placed upside down onto the receiving substrate, previously patterned with IDEs. Kapton polyimide thin films were used as spacers between the donor and receiving substrate. The image from the CCD camera was used to help position a single nanowire on the donor substrate over top of the IDEs. Once the desired position was achieved, a single laser shot was fired to propel the nanowire onto the IDE array below, as shown in Figure 2. All laser transferred

materials were characterized using optical microscopy (BX51, Olympus Corp.).

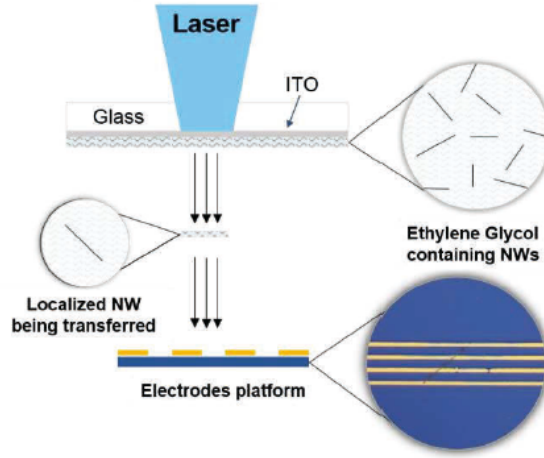


Figure 2. Schematic depicting the setup for LIFT of SnO_2 nanowires suspended in ethylene glycol where the donor substrate is an ITO-coated glass slide and the receiving substrate is an oxidized silicon chip with patterned Au IDEs (width = 2 μm).

3. RESULTS & DISCUSSION

3.1 LIFT using a PDMS patterned release layer

The ability to rapidly print small scale features (microns) over a large area with high precision is important for numerous applications. To accomplish this, Ag nanoink was laser transferred using a PDMS donor substrate with microwells. This donor substrate is reusable by simply rinsing the surface with isopropanol (IPA) to remove any nanoink residue, without degradation of the PDMS. The PDMS donor substrate can be seen in Fig. 3(a), where the microwells are unfilled. After dosing the substrate with Ag nanoink, it can be seen that the wells fill without excess Ag on the PDMS surface. This can be seen in Fig. 3(b), where the filled microwells are seen to the upper left and unfilled microwells are seen in the lower right portion of the donor substrate. By utilizing a laser spot size that is larger than the microwells, multiple Ag microdrops can be printed at one time. For example, a 100 μm Gaussian laser spot can transfer ~ 50 Ag microdrops, depending on microwell spacing. It is possible to use a larger laser spot size to print even more features at once; however, the laser fluence will decrease as spot size is increased so there is a maximum spot size at which nanoink will not release from the substrate due to insufficient laser energy.

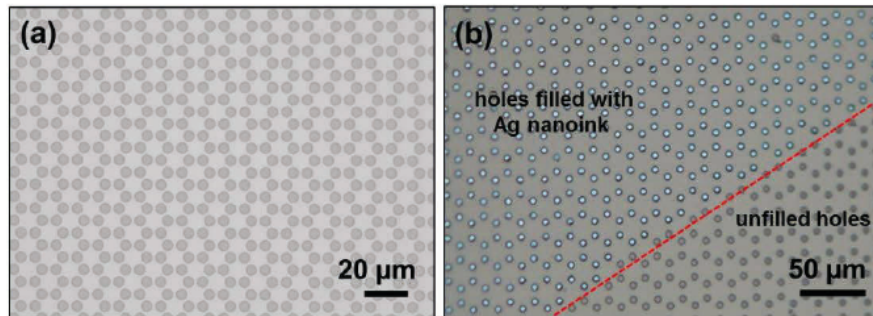


Figure 3. Optical micrographs of a PDMS donor substrate with (a) unfilled circular microwells ($\sim 5 \mu\text{m}$ diameter) and (b) microwells filled with Ag nanoink.

The transferred Ag nanoink microdrops can be seen in Figure 4, where it is clear that the transferred drop size is $\sim 1 - 2 \mu\text{m}$ in diameter. This is significantly smaller than the PDMS microwell size of $5 \mu\text{m}$. This discrepancy could be due to the incomplete transfer of all of the material in the microwell onto the receiving substrate surface. In addition, surface tension could be forcing the microdrops to maintain a high contact angle with the PDMS receiving substrate, making their diameters smaller. Because similar processes can be used to stamp inks onto receiving substrates, we confirmed that the droplets were not deposited via stamping but indeed due to laser printing. This technique allows for the simultaneous printing of multiple micro-features (few microns) with a single laser shot without damaging the donor substrate. The PDMS donor substrates were simply rinsed with IPA, dried with nitrogen and reused without any visible damage to the PDMS itself.

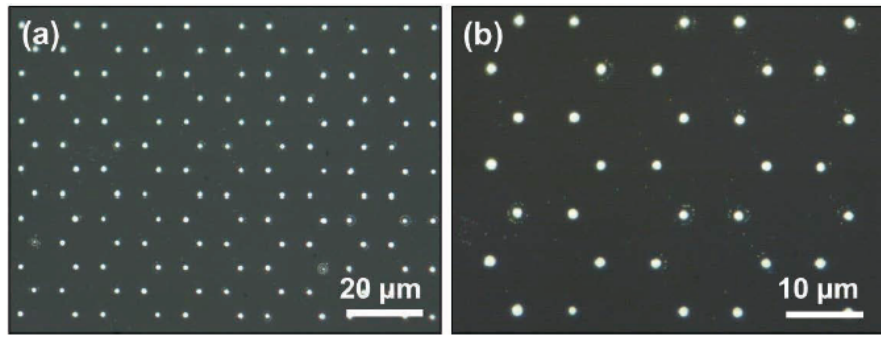


Figure 4. (a) Low and (b) high magnification micrographs of laser printed Ag nanoink (cured in oven at 125°C for 30 min) onto a PDMS receiving substrate using a reusable PDMS donor layer.

Several advantages are gained by using this approach compared with traditional LIFT processing, which involves a donor substrate that is not patterned with micro features. In most previous work, a glass substrate, which is UV-transparent, is coated with the Ag nanoink and laser pulses are fired individually in a serial manner to print the desired pattern. By utilizing a patterned release layer, the ease of printing small features becomes a primary advantage in that printing becomes a parallel process. Also, printing structures that are $\sim 1 - 2 \mu\text{m}$ is difficult using traditional LIFT because of limitations of the optical system. By using a patterned release layer, printing of these small micro-scale features and even nano-scale features becomes possible. Additionally, this technique significantly reduces the amount of debris seen on the receiving substrate that is due to splashing as a result of impact. The laser fluence required to transfer Ag nanoink using traditional LIFT processes has been documented in a previous publication¹⁸, and was found to be between $\sim 29 - 66 \text{ mJ}/\text{cm}^2$. Alternatively, the laser fluence needed for successful transfer of Ag nanoink from patterned PDMS release layers is $\sim 95 \text{ mJ}/\text{cm}^2$. This discrepancy is likely due to the thickness of the Ag layers being printed and the geometry of the nanoink layer. The Ag nanoink layer used in traditional LIFT was $\sim 1 \mu\text{m}$ thick, whereas the microwells used to print the Ag microdrops were $\sim 5 \mu\text{m}$ deep. The microwells also confine the nanoink on all sides, unlike a thin, uniform layer of ink. Thus the Ag microdrops printed using the patterned PDMS layers require more laser energy to release the material.

3.2 LIFT of nanowires using an ITO donor layer

In addition to the ability to print solid metal foils and Ag nanoink using reusable elastomeric donor layers, metal nanowires were printed using a ceramic reusable donor layer. The donor

layer for these experiments was an ITO-coated glass substrate, whereas the nanowires were SnO₂. The motivation for this work was to investigate if the selection of single nanowires and assembly onto a specific location (IDEs or MEMs devices) could be achieved for potential high-throughput characterization and device fabrication. Currently, chemiresistive MOS research has been limited by complications associated with the manipulation of these novel structures (e.g. nanowires, 2D materials) or by the labor-intensive assembly processes for studying the newly synthesized nanoscale materials. Because of the fragility and small size of nanowires, placement of an individual nanowire onto electrodes can be challenging. By using LIFT in conjunction with the ITO reusable donor layer, single nanowires can be placed onto the patterned electrodes with high precision without damaging the nanowire, receiving substrate or ITO donor layer. The ability to print a single nanowire with high precision and no degradation to the nanowire or donor substrate opens the possibility for creating highly sensitive gas sensor devices with applications in science, environmental monitoring, medicine and national security. For the successful transfer of individual nanowires, an image of the IDEs on the receiving substrate was superimposed on the image of the nanowires suspended in ethylene glycol. The donor substrate was aligned manually until an individual nanorod was positioned on top of the electrodes. Since this procedure was performed by hand, it was difficult to get perfect alignment (see Figure 5). However, the alignment is sufficient for the future electrical characterization of a single nanowire.

Once the alignment procedure was performed, a single laser shot with a spot size of 100 μm was used to propel the nanostructure onto the IDEs, presumably due to the rapid thermal expansion of the energy absorbing ITO layer and the evaporation of the ethylene glycol surrounding the nanowire. The transfer was performed instantly without any deviation from the initial alignment. The effect of laser fluence on the reusability of the ITO donor layer was studied and shows that there exists a threshold where damage is observed. The damage threshold appears to be around $\sim 400 \text{ mJ/cm}^2$, with optimal laser transfer occurring at $\sim 270 \text{ mJ/cm}^2$. Previous studies⁸ using ITO as a release layer show that similar laser fluences cause damage to the ITO layer when trying to release solid Cu foils. This is likely due to varying UV-transparency between the ITO films used. The manufacturing process used to fabricate nanowires provided us with a highly heterogeneous population of rod-like structures that range from tens of nanometers to hundreds of nanometers in diameter. Due to limitations in the resolving power of the optical system described above, the successfully transferred SnO₂ nanowires averaged 17.5 μm in length and 500 nm in diameter.

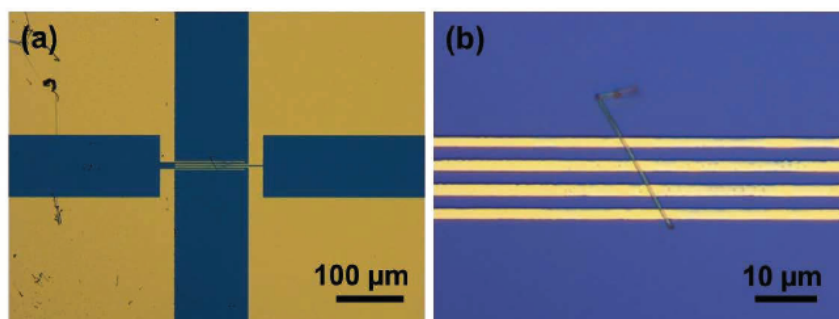


Figure 5. (a) Patterned Au inter-digitated electrodes (IDEs) on a Si wafer with a thermal oxide layer and (b) higher magnification of IDEs showing an individual laser printed SnO₂ nanowire.

4. SUMMARY

Laser-induced forward transfer (LIFT) as a rapid prototyping tool enables the fabrication of various structures, including microelectronics and sensors. By utilizing a patterned PDMS donor layer, Ag nanoink microdrops can be printed over a large area with high precision and speed. In addition, metal nanowires can be printed onto patterned IDEs using an ITO donor layer. Both of these donor layers are reusable and remain undamaged during processing allowing for laser printing of a wide variety of materials and microstructures.

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