

Alexandra Palla Papavlu and Thomas Lippert

## CONTENTS

13.1 Introduction .....	149
13.1.1 LIFT with a Sacrificial Layer .....	150
13.1.2 LIFT of Liquids .....	152
13.2 LIFT in Science: Examples of Materials and Devices Transferred by LIFT .....	153
13.3 LIFT in Industry .....	156
13.4 Conclusions and Future Directions .....	157
Acknowledgements .....	157
References .....	157

**13.1 Introduction**

Nowadays the field of electronics, in particular the fabrication of integrated circuits, micro- and nanodevices, is dominated by various microfabrication processes, in particular by lithography technologies. These technologies are used to fabricate different-sized patterns, from the nanoscale, i.e. from few nanometres, to the mesoscale, i.e. micrometres to millimetres, which ultimately may be arranged in various architectures to create complex structures.

Depending on the fabrication technology source type, i.e. applications envisioned, the majority of the lithography techniques fall into two categories: techniques that require masks or moulds (such as photolithography, [1] soft lithography [2], and nanoimprint lithography (NIL) [3]) and direct write techniques (such as electron beam and focused ion beam lithography [4,5], scanning probe lithography [6], screen printing, inkjet printing) or laser direct write techniques (such as laser-induced forward transfer (LIFT)) [7].

The use of laser direct writing methods, in particular LIFT for printing various materials and its ability to integrate dissimilar materials into devices, is the fulcrum of this chapter. Therefore, first, we will briefly introduce the conventional printing techniques, showing their advantages and limitations, followed by a brief history of the laser direct writing methods, i.e. LIFT, ultimately showing few examples of its variations and some of the most successful applications.

*Photolithography* is the main technique used in industry for pattern transfer and microdevice fabrication. Depending on the working principle, photolithography may be divided into contact, proximity, and projection lithography. Contact and proximity photolithography relies on the exposure of a polymer, i.e. a photoresist to UV light, through a photomask which allows the definition of the desired pattern. Photolithography is a multistep process – i.e. firstly, a thin film of photoresist

is coated onto a substrate, and then the photomask with the desired pattern is positioned above the photoresist (in contact, close proximity, or projection). The photoresist that is not covered by the photomask is illuminated with UV light and becomes soluble or insoluble, and the photoresist that is covered by the photomask may be removed (or remains) in a subsequent dissolving step.

Projection photolithography is a technique in which a system of optical lenses is used which focus the UV light onto the photoresist, thus allowing the reduction of the patterns to few nanometres [8].

*Soft lithography* is a class of techniques applied for rapid prototyping micro- and nanoscale structures and devices. There is a large number of techniques, e.g. microcontact printing [9], replica moulding [10], microtransfer moulding [11], and nanotransfer printing [12], just to name a few, which fall into the soft lithography category. All these techniques are basically based on printing, moulding, and embossing with an elastomeric stamp.

Similar to soft lithography, NIL utilizes a stamp, mould, master, template, or shim to physically deform a polymer for nanoscale patterning [13]. In order to achieve high throughput and high resolution at a relatively low cost, nowadays different versions of NIL, i.e. thermal wafer-scale NIL, UV wafer-scale NIL, UV step, and repeat NIL and roll-to-roll printing, have emerged.

*Electron beam and focused ion beam lithography* complement the main fabrication techniques for nanoscale patterns. These techniques use either an electron beam or a focused ion beam (e.g. gallium ions) to scan the surface of a sample. The high resolution of the techniques, i.e. 2–20 nm, makes them appealing for applications in microelectromechanical systems (MEMS) or protein engineering.

*Scanning probe lithography* utilizes a sharp scanning probe (most of the techniques use the tip of an atomic force

microscope (AFM)) to heat, scratch, oxidize, or transfer material to a surface for patterning nanoscale features [14]. The most common of the scanning probe lithography methods is the dip-pen nanolithography technique, which relies on coating the probe of an AFM with the material to be transferred, i.e. ink, polymer, and upon contact with a surface, deposits the material. This approach is used in a variety of applications, including surface assembly, nanoelectronics, and cell–surface interactions [15].

These techniques, although allowing patterning with ultra-high resolution, i.e. down to few nanometres, are limited in industrial applications, for mass production. In contrast, direct write techniques such as screen printing and inkjet printing are widely used for mass production; however, their lateral resolution lies in the micrometre range, e.g. around 70  $\mu\text{m}$  in the case of screen printing.

*Screen printing* is a low-cost technique in which a paste or a precursor of the material to be transferred is applied onto a steel mesh (i.e. the screen) which is pre-patterned with the desired feature. The paste or precursor is pressed with force through the screen, thus transferring the pattern onto the substrate. This technique has the advantage that thick layers can be realized.

To date, *inkjet printing* is the most popular printing technology. This technique relies on the production of droplets containing the material of interest, which are propelled through a nozzle onto a substrate. Depending on the mechanism of transfer, there are two categories of inkjet printing technologies: continuous inkjet and drop-on-demand. Continuous inkjet printing is based on the continuous generation of droplets, which makes it a rather wasteful process and thus is not widely used. In contrast, drop-on-demand inkjet printing is simpler than continuous inkjet printing, and droplets are ejected on demand.

Despite the advancements in classical printing technologies, there are still many challenges to surmount. For example, most of these techniques are not flexible as they use cylinder, masks, and screens. In addition, the use of solvents is also an issue for applications which require the fabrication of multilayers. Finally, there is a stringent need for new materials with tailored properties, and alternative sintering and curing techniques so that heat addition to the printed flexible substrates can be kept minimal.

Since the invention of the first laser in 1960, laser-based techniques and related applications have developed rapidly. Nowadays, lasers are standard tools in different fields, i.e. in industrial processes like cutting or welding, in medicine for eye surgeries, or tattoo removals. Moreover, recently, the laser-based techniques used in microfabrication and microstructuring applications [16] are close to the transition from the research laboratories to industry.

One of the laser-based techniques used for microfabrication applications, which has drawn a lot of attention over the years, is laser-induced forward transfer (LIFT). LIFT is a direct write method, initially developed for the graphics industry, to write inks to glass substrates [17,18]. In 1986, Bohandy et al. were the first to use LIFT to transfer Cu metal films from a quartz substrate with an excimer laser working at 193 nm, first in vacuum and one year later in air [19].

The basic principle of LIFT is rather simple; i.e., the material to be printed is spread as a thin film (named the donor film) onto a substrate which is transparent to the laser radiation (also known as the donor substrate). The laser beam is either focused or imaged through the donor substrate onto the donor film (see Figure 13.1a). Each laser pulse interacts with the donor film material, and with a high enough laser energy per pulse, the material is delaminated from the donor substrate and is transferred onto the receiver substrate placed parallel and in close proximity to the donor. The shape and dimension of the transferred material is determined by the shape of the laser beam. The entire donor–receiver system is placed onto a xyz stage, thus allowing the transfer of arbitrary patterns onto the receiver substrate. In addition, another advantage of LIFT is that the process is carried out in air and at ambient temperature, without any additional photolithography step.

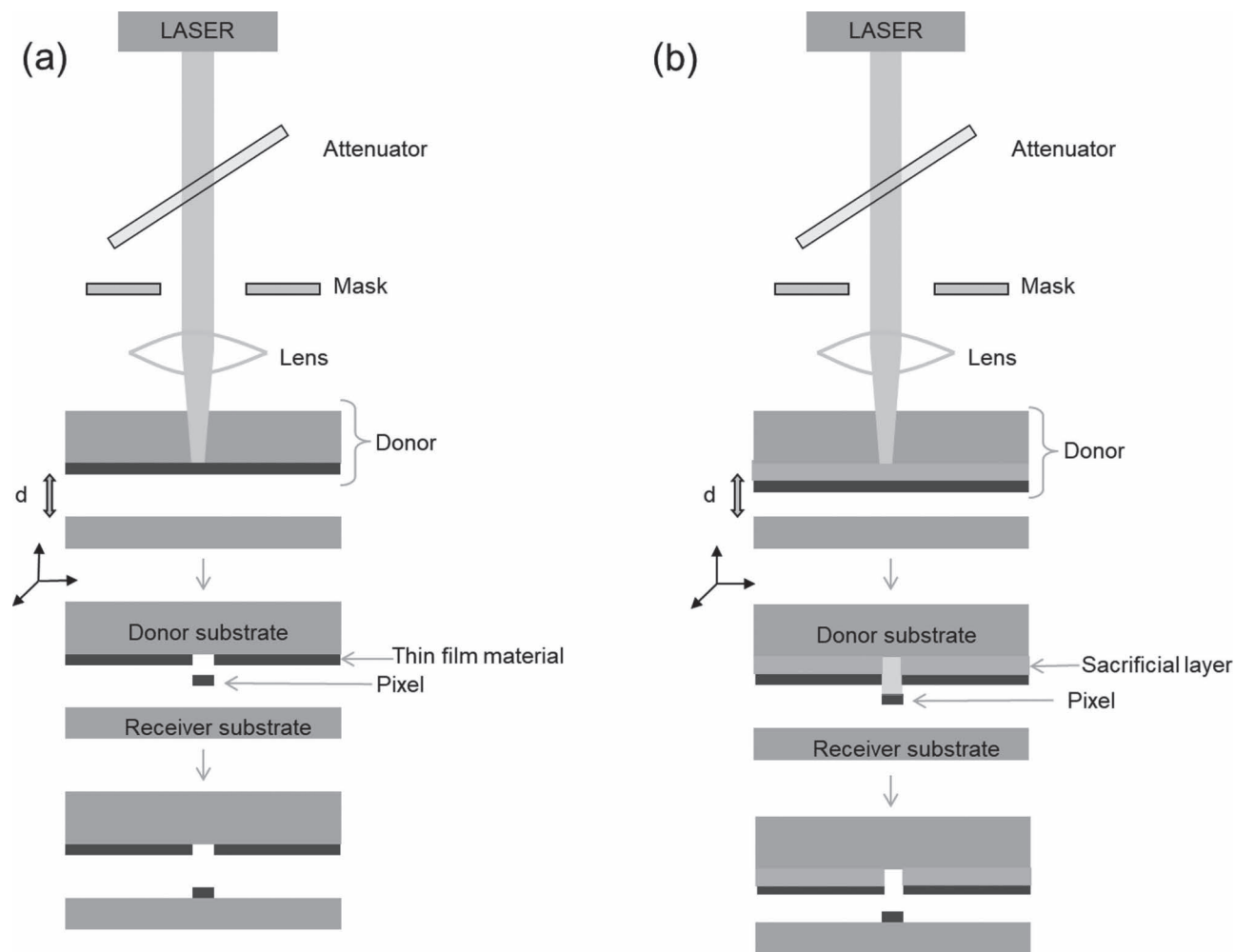
Conventional LIFT, i.e. with the material to transfer directly deposited onto a transparent donor support, works well for inorganic materials such as metals or ceramics, e.g.  $\text{Al}_2\text{O}_3$  [20]. However, soft materials, e.g. polymers, proteins, cells, and tissues, or more complex materials such as superconductors can be transferred using different variations of LIFT, in which an additional layer is added to the donor system between the material to transfer and the transparent support. This is due to the fact that soft materials may be damaged by the laser beam during transfer due to thermal or photochemical decomposition. In addition, an interlayer that absorbs the laser radiation is needed in case of none or weakly absorbing materials, where standard LIFT proves to be difficult. Therefore, in the literature, there are various reports on LIFT with an additional light-absorbing layer. This layer, on the one hand, absorbs the laser radiation and at the same time shields the material of interest from the laser light. Various names have been given to LIFT with an interlayer between the material to transfer and the transparent support, e.g. blister actuated LIFT [21], dynamic release layer (DRL) LIFT [22], and absorbing film-assisted (AFA) LIFT [23], just to name a few. A sketch of LIFT with an interlayer in the donor system is shown in Figure 13.1b.

### 13.1.1 LIFT with a Sacrificial Layer

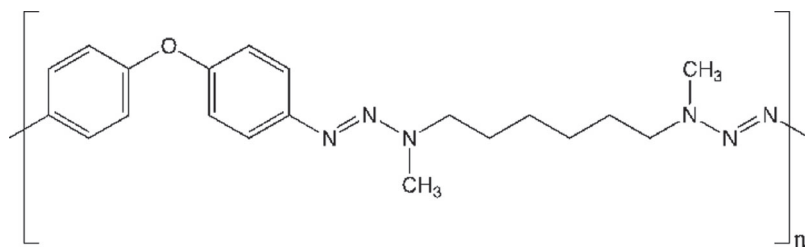
The first LIFT experiments using an additional interlayer were carried out in 1993 [24]. The authors of the study used an aluminium thin film as an interlayer, which they named light-to-heat conversion layer due to the transfer mechanism which was purely thermal [25]. Later studies showed the successful transfer of different materials with metal interlayers, also known as sacrificial layers. The basic principle relies on superheating the metal interlayer with the laser beam, generating a plasma which expands, and thus, the material on top is ejected.

Another variation of LIFT is using polymer thin films as a sacrificial layer. One class of polymers used as DRL or sacrificial layers is represented by photodegradable polymers, e.g. polymers that incorporate the triazene unit into the backbone. The chemical structure of the triazene polymers is shown in Figure 13.2.

In the case of the TP used as a DRL, the photons break specific chemical bonds and thus decompose the polymer completely into gaseous products initiating the forward



**FIGURE 13.1** The basic principle of LIFT (of solid thin films). (a) The laser is focused at the interface transparent donor substrate – material to be transferred. The material is heated by the laser light, and due to the heat expansion, a flyer is ejected. (b) The laser is focused at the interface transparent donor substrate – sacrificial layer. The sacrificial layer absorbs the laser radiation, at the same time shielding the material of interest from the laser light, and transfers the material on top onto the nearby receiver substrate.

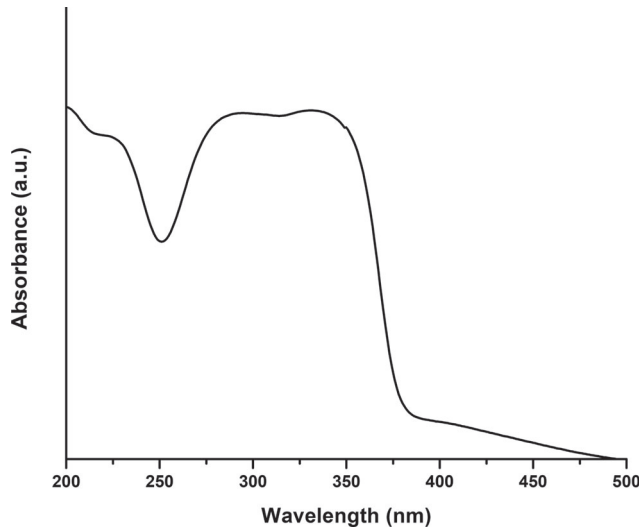


**FIGURE 13.2** Chemical structure of the triazene polymer used as a DRL in most of the LIFT experiments.

transfer of the material of interest. One of the advantages of the TP is the fact that they absorb and decompose between 150 and 360 nm, making them well suited for irradiation with different wavelengths of laser [26]. Two absorption maxima can be distinguished in the UV-VIS absorption spectrum of a typical triazene polymer thin film, one around 200 nm which can be assigned to the aromatic system and one around 330 nm which corresponds to the triazene unit, as shown in Figure 13.3 [27].

Adjusting the TP thickness to achieve a well-defined transfer made it possible to transfer a wide range of materials and functional devices, from polymers for sensors [28], biomaterials [29], cells in a polymer matrix [30], and organic light-emitting diodes (OLEDs) [31].

Following the works on LIFT with an intermediate layer, a new approach was developed, based on chemically unstable materials that decompose upon absorption of UV radiation. This technique was named reactive LIFT [32], and it was



**FIGURE 13.3** UV-VIS spectra of the triazene polymer thin film spin-coated onto a fused silica plate.

used for the transfer of metal oxide semiconductor materials aiming at sensor applications [33]. Tin oxide was transferred by an irradiation of a metal complex precursor material, i.e. acetylacetonate  $\text{SnCl}_2(\text{acac})_2$ , with a 308 nm laser beam. Upon irradiation, the  $\text{SnCl}_2(\text{acac})_2$  acts as a DRL and partially decomposes to  $\text{SnO}_2$ . These materials are particularly appealing due to fact that they are cheap, have low deposition temperatures, are ideal for implementation onto flexible substrates, and present an excellent potential for scaling-up.

### 13.1.2 LIFT of Liquids

The implementation of LIFT that can compete on an equal basis with the more conventional direct writing techniques is expected to advance the state of the art within the fields of microelectronics for the fabrication of devices (sensors or OLEDs) and also biology for microarray fabrication or tissue engineering. The possibility of LIFT to print directly not only solid materials but also fluids from thin liquid films can direct the future industrial implementation of the technique as a realistic goal. In addition to this, in this section we will show that with LIFT, it is possible to print liquid materials with a resolution in the order of one or several micrometer(s). Thus, with liquid-phase LIFT, it is possible to obtain comparable levels of integration to the usual photolithography, with consequent advantages in terms of speed and flexibility. While the latter is at a higher stage of development, LIFT has significant advantages for the fabrication of microarrays: no problems related to printing head (nozzle) clogging or tips cleaning, only minor limitations on the rheological properties of solutions to deposit, and the ability to work with lower sample volumes.

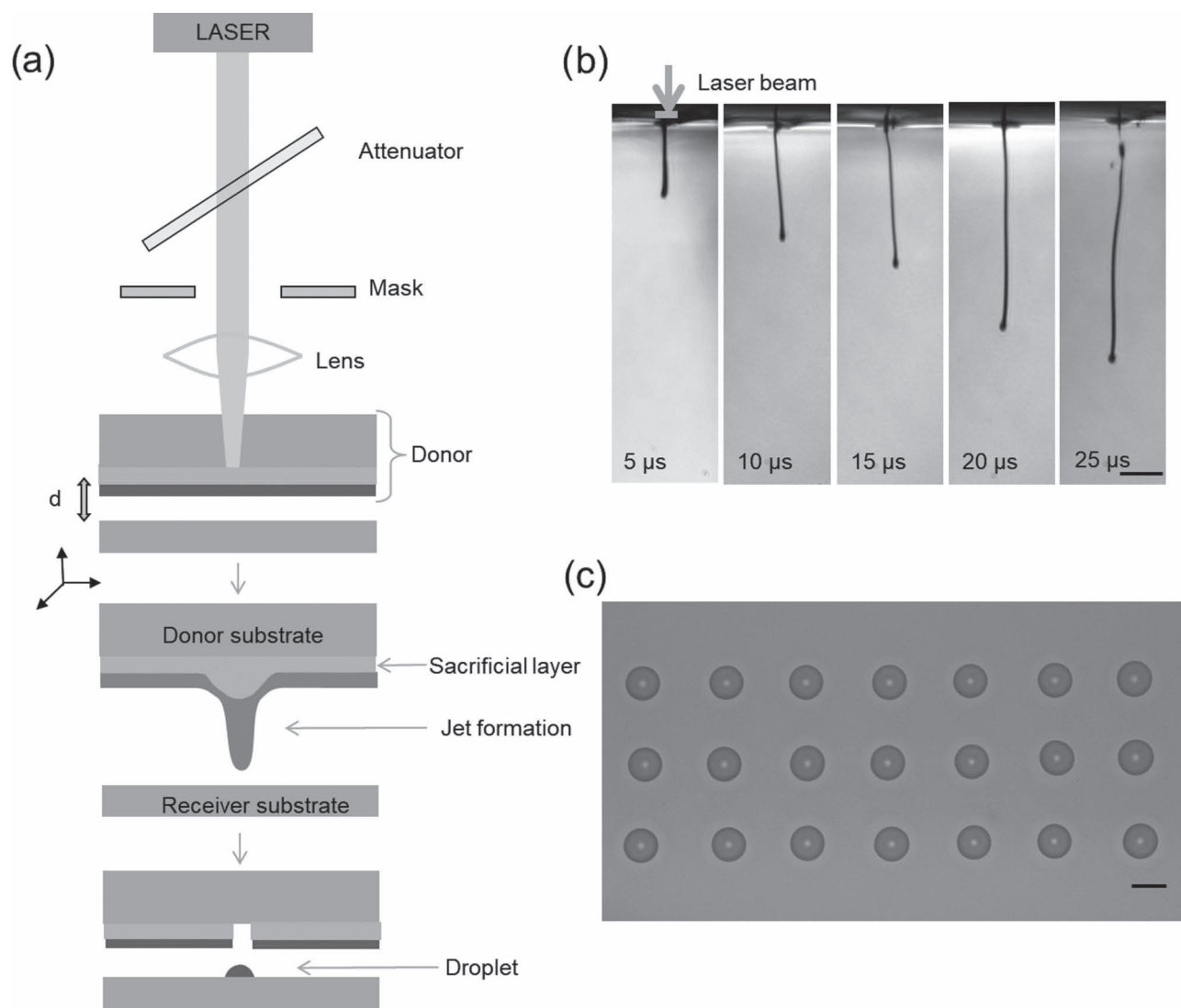
Demonstrations of LIFT using liquid donor films with different DRLs are reported in the literature. A large number of functional materials have been transferred by LIFT aiming at applications in chemical sensors [34], biosensors, or tissue engineering, e.g. proteins [35,36], DNA [37], cells [30], and even tissue [38].

In addition to the works presented above, studies on the ejection mechanism in the case of LIFT of liquids have been carried out and a completely different behaviour to the case of solids has been found. The principle of LIFT for material transfer in a liquid phase is shown in Figure 13.4a. In the case of LIFT of liquids, both with polymers and with metal DRL layers, the transfer mechanism is dominated by the formation of long needle-like jets (see Figure 13.4b), which upon contact with the receiver substrate form sessile droplets. Liquid-phase LIFT is driven by the formation and expansion of a high-pressure vapour bubble. This bubble is attributed to the plasma formed after laser ablation of the metal DRL layer. The bubble expansion process can result in three different situations depending on the applied laser fluence. At low fluences, a needle-like jet is developed; however, this jet has not enough energy to overcome the surface tension forces, and thus, the jet does not reach the receptor and no material is transferred. At intermediate fluences, the same jet is formed, but in this case, it advances at a constant velocity while getting thinner. At high fluences, the bubble expansion is so violent that it overcomes the surface tension, resulting in bubble bursting. This is a situation which generates splashing on the receptor substrate [39,40]. A series of time-resolved images of liquid jets is presented in Figure 13.4b.

Conventional LIFT for liquids has emerged over the last years as a powerful technique for printing a wide class of biomaterials in particular for the fabrication of microarrays (see Figure 13.4c), being an interesting alternative to other printing techniques, since it is free from the clogging problems characteristic of inkjet printing, and also from the contamination issues usually associated with the incorrect cleaning of pins in dip-pen printing. In addition, LIFT allows achieving higher degrees of resolution. However, it presents the drawback of requiring the preparation of the liquid to be printed in thin film form, which limits its possibilities towards industrialization.

In the studies reported in Ref. [41] a new idea for a laser-based technique allowing the direct printing of biological solutions without the need for preparing the liquid in thin film form has been developed. Thus, the main drawback of conventional liquid LIFT can be overcome. The new technique allows a significant improvement in micropatterning in terms of control, reproducibility, and resolution.

The operating principle of this new technique relies on strongly focusing a femtosecond pulsed laser beam inside the liquid to be printed just below the free surface, so that the laser pulse energy is absorbed in a tiny volume around the focal point. This generates a cavitation bubble that projects a small fraction of the liquid beyond the free surface, and the liquid is deposited on a substrate as a printed droplet. The displacement of the substrate with respect to the free surface allows the realization of micropatterns. In order to obtain the proper absorption, two conditions are mandatory: (i) The liquid must be either transparent to or weakly absorbing of the laser radiation; otherwise, the absorption would take place right at the surface and not below. This condition is fulfilled by almost any biomolecule solution. (ii) The laser beam must be tightly focused, so that absorption occurs in the beam waist and not in the rest of the beam path.



**FIGURE 13.4** (a) The principle of LIFT (the material of transfer is in the form of a liquid layer). (b) Time-resolved images of TP-LIFT. The laser used for irradiation is the XeCl (308 nm), the TP layer is 60 nm, and the laser fluence is  $25 \text{ mJ cm}^{-2}$ . Scale bar is  $500 \mu\text{m}$ . (c) Optical microscopy image of a microarray printed by TP-LIFT (TP thickness is 60 nm) on glass at  $25 \text{ mJ cm}^{-2}$ . Scale bar is  $50 \mu\text{m}$ .

However, one of the main disadvantages of this technique is the use of femtosecond laser, which, at present, makes it a rather expensive alternative.

## 13.2 LIFT in Science: Examples of Materials and Devices Transferred by LIFT

Since the first experiments of LIFT, this technique was successfully applied for the transfer of various materials both in solid and in liquid phase as well as complex materials which were ultimately integrated into functional devices. Below we will show a few examples of some of the materials transferred by LIFT and several other variations of the technique and also a few examples of functional devices fabricated with this method.

One of the most popular variations to LIFT is matrix-assisted pulsed laser evaporation – direct write (MAPLE-DW), a

process similar to the matrix-assisted pulsed laser evaporation (MAPLE), which in turn is derived from the classical pulsed laser deposition (PLD) [42]. MAPLE is an organic thin film deposition technique, where the material of interest, a biological compound, or polymer is suspended into a solvent and the resulting solution is flash-frozen in liquid nitrogen in order to obtain a solid target [43]. This target is then irradiated with a laser beam, as in the case of PLD. MAPLE-DW has the advantage of MAPLE; i.e., it can be applied to most soft materials, combined with the lateral resolution of LIFT. MAPLE-DW has been mostly used for the transfer of polymers and organic compounds, including also some devices, such as batteries and sensors [44].

More recently, a technique similar to MAPLE-DW has been reported, namely laser decal transfer (LDT), which has been used to transfer custom metallic nanoinks [45] aiming at applications such as microbridges and microcantilevers [46,47]. With LDT, mostly high-viscosity nanoparticle suspensions

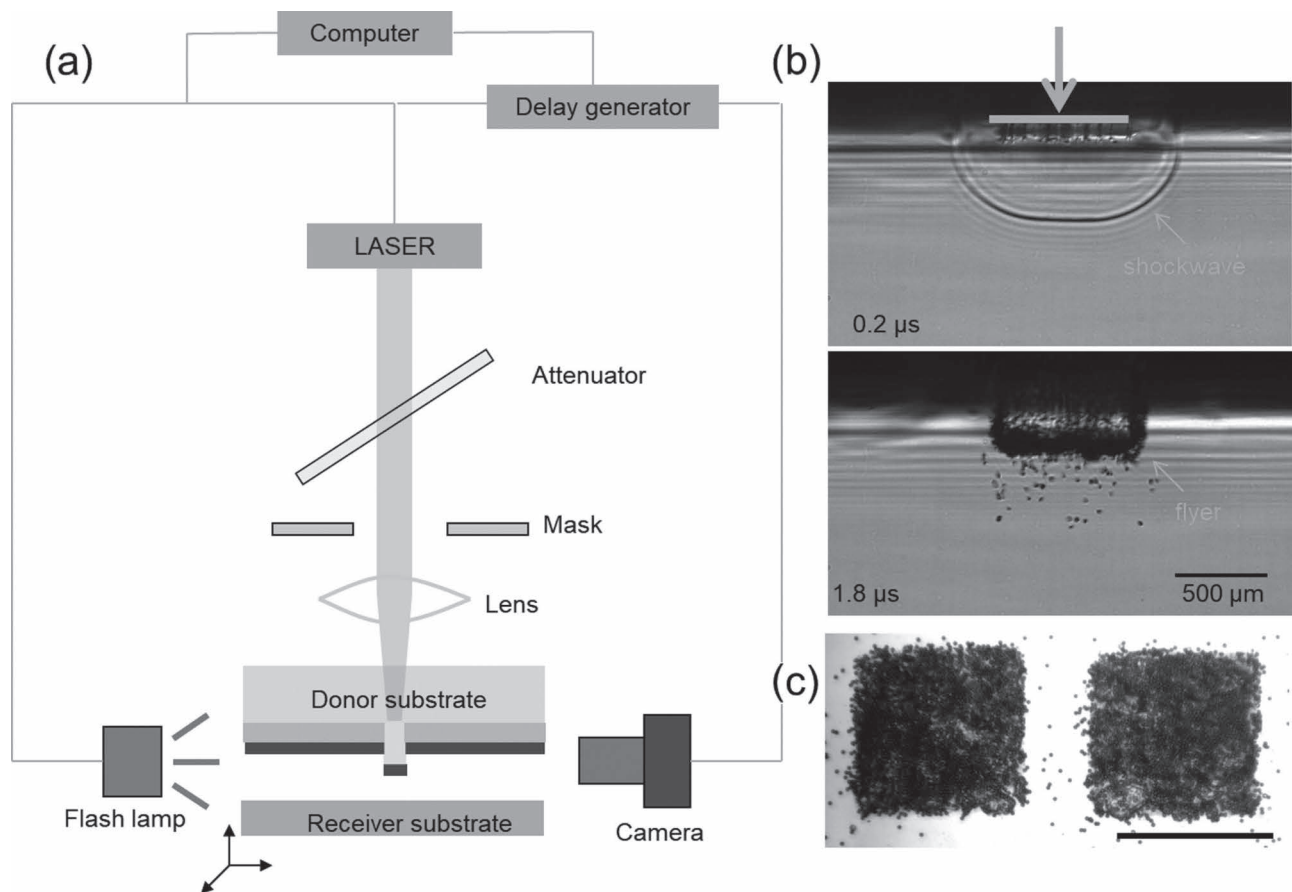
(1000–100 000 cP) were used as inks for the fabrication of the donors, unlike most of the works by other groups [48], where the nanoinks used in laser transfers have viscosities lower than 100 cP. In addition, this technique has been successfully proven for the fabrication of three-dimensional stacked structures [49].

A first example of successful solid material transfer with LIFT using a polymer intermediate layer, i.e. a triazine polymer, is the fabrication of polystyrene microbeads (PS- $\mu$ beads) microarrays on Thermanox coverslips, which can ultimately be applied in biochip applications. TP layers of 100 nm were used to propel close-packed monolayers of PS- $\mu$ beads, which do not suffer any chemical decomposition during transfer [50,51]. In the same study, an investigation of the transfer dynamics is shown; i.e. the authors use shadowgraphy imaging to get an insight into the transfer mechanism following the laser pulse. A scheme of the set-up for time-resolved imaging experiments for LIFT is shown in Figure 13.5a, while in Figure 13.5b and c, two pictures taken for back-side ablation of a PS- $\mu$ beads pixel on top of a 100-nm-thick triazine polymer layer together with the corresponding optical microscopy images of the pixels transferred are shown.

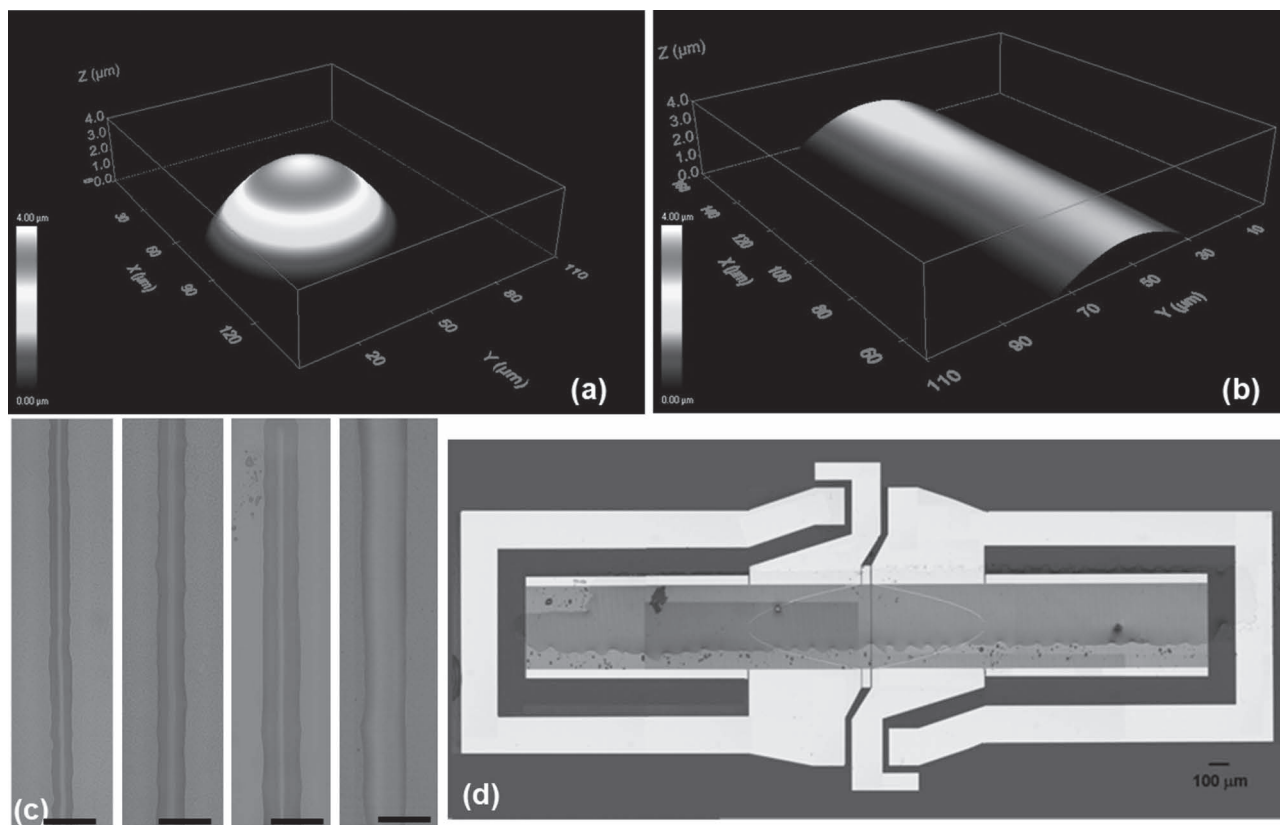
Another important field of application for LIFT and its variations is printing of different inks and pastes for the printed electronics industry. LIFT comes as a direct competitor of inkjet

printing, which despite being a leader in the field, still presents some limitations mainly related to printing head clogging, resolution, and customized inks, just to name a few. Several studies have focused on the potential of LIFT for printing lines from different donor materials. One of the first examples where the possibility of printing long lines from liquid-phase donor materials by varying the distance between successive droplets is presented in Ref. [52] (see Figure 13.6a–c). Other studies focused on demonstrating the successful printing of silver lines narrower than 20  $\mu\text{m}$ , which have a resistivity lower than 20  $\mu\Omega\text{ cm}$  [53,54].

More recently, a number of studies from the group of P. Delaporte [55,56] have been focused on printing silver lines by LIFT and also on the investigation of the dynamics of the process in LIFT of silver inks. First, in Ref. [57], they showed the successful transfer by LIFT of conductive 20  $\mu\text{m}$ -width silver lines at a velocity up to 4  $\text{m s}^{-1}$  in three passes. Then, they demonstrated that they could print a continuous line in a single-step process by reaching velocities up to 17  $\text{m s}^{-1}$ . Moreover, they carried out fundamental studies on the laser transfer process and found that below a minimum distance between two successive laser spots, it is not possible to print features with a high resolution, and in addition, high printing velocities do not allow the overlapping of the droplets and the single-step printing of a continuous line.



**FIGURE 13.5** (a) Set-up for time-resolved imaging experiments for LIFT of solid donors. (b) Sequence of photographs taken for back-side ablation of a microbead array on top of a 100 nm triazine polymer film at  $1.5\text{ J cm}^{-2}$  laser fluence. (c) Two microbead pixels printed by LIFT at  $2\text{ J cm}^{-2}$  (left-hand side image) and  $1\text{ J cm}^{-2}$  (right-hand side image) laser fluence. Scale bar is  $200\ \mu\text{m}$ .



**FIGURE 13.6** Confocal microscopy images of (a) a water:glycerol (50% v/v) droplet printed by LIFT, (b) a uniform water:glycerol (50% v/v) line obtained by printing successive individual droplets. (c) optical microscopy image of uniform lines. Printing direction is from top to bottom, and scale bar is 100  $\mu\text{m}$ . (d) Optical microscopy images of a SAW device coated by overlapping droplets (20% v/v OBP solution) printed by LIFT at  $700 \text{ mJ cm}^{-2}$  laser fluence.

Further on, LIFT has been extensively used for the fabrication of sensors, and the following paragraphs briefly present few examples of the achievements.

A surface acoustic wave e-nose has been fabricated by printing different polymers, i.e. polyethylenimine, polyepichlorohydrin, polyisobutylene, hydroxypropylmethyl cellulose, and poly(styrene-co-maleic acid), partial isobutyl/methyl mixed ester on the interdigitated transducers of SAW devices. The functionality of the SAW e-nose was demonstrated by its ability to detect low concentrations of analytes (dichloromethane, dichloropentane, dimethyl methylphosphonate, ethyl acetate, and water) and also to discriminate between the tested analytes. The results obtained in Ref. [58,59] indicated that laser deposition of polymers onto SAW resonators is possible without significant modifications of their functionality and with a good reliability and reproducibility.

Not only sensors in solid phase, but also biosensors may be fabricated by LIFT, as it has been shown by Touloupakis et al. [60] and Palla Papavlu et al. [61]. Touloupakis et al. have demonstrated the successful fabrication of electrochemical-based biosensors for the detection of diuron and linuron herbicides. They used thylakoid proteins as active materials which were directly immobilized (taking advantage of the high pressures achieved during LIFT) onto the metal electrodes of the biosensors, thus eliminating an additional functionalization step.

In Ref. [62] a SAW biosensor array composed of SAW devices coated by LIFT with different odorant-binding proteins (OBPs) (see Figure 13.6d for an example of a SAW biosensor printed with a solution containing OBPs) has been described. The biosensor system was tested in  $\text{N}_2$  atmosphere upon exposure to vapours of octenol (also called mushroom alcohol, is an enantiomer produced by several plants and fungi) and carvone (an enantiomer that smell like spearmint).

A last example of successful material printing by LIFT aiming at applications in the microelectronics field is presented below. Most of the applications envisioned target the domain of organic electronics, specifically the fabrication of OLEDs and organic thin film transistors (OTFTs). Different materials have been printed, e.g. organic semiconductors (CuPc, poly(3,3'-didodecylquaterthiophene) (PQT-12), poly(3-hexylthiophene-2,5-diyl) (P3HT), distyryl-quaterthiophene (DS4T), bis(2-phenylthynyl) end-substituted terthiophene (diPhAc-3T), pentacene), and different metal nanoparticle inks or polymers such as poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT: PSS) for the fabrication of the source and drain electrodes in OTFTs. Although OTFTs have been realized using other printing techniques, their laser printing has so far proven to be the only digital technique that works well with a wide range of materials. In our particular case, the OTFTs obtained by laser printing exhibited good electrical performances, with mobilities of few  $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

and  $I_{\text{on}}/I_{\text{off}}$  of the order of  $10^5$ . However, the laser printing process can also come with some drawbacks, such as the induction of mechanical stress or the structural reorganization of the material. In this context, the LIFT technique can be particularly attractive for the printing of organic materials having high structural cohesion.

The laser printing process has been successfully applied also for the fabrication of OLEDs, in particular polymer light-emitting diodes (PLEDs). Two main approaches have been considered to this end: (i) the single-step transfer of a solid multilayered stack [31,63] and (ii) the printing of an active organo-metallic material in liquid phase between two electrodes, as reported by the group of C. Arnold. In both of these instances, the use of a sacrificial DRL has proven to be mandatory in order to avoid the thermal or photochemical degradation of the luminescent material. As such, red-green-blue (RGB) pixels of PLEDs have been successfully achieved through the single-step transfer of a multilayered structure, without the loss of device performance. The functional properties of the obtained PLEDs (e.g. luminance, efficiency) are comparable to those of conventionally fabricated devices, while in the case of blue pixels, it was found to surpass them. For the electroluminescent devices printed in liquid phase, their testing in air revealed that the emission spectra, luminous efficiencies, and lifetimes are similar to those of devices fabricated in nitrogen environment. Multi-colour lumiphore patterns with diameters down to  $10\ \mu\text{m}$  have also been printed with laser direct write, thus demonstrating the versatility of the technique [56,64].

To conclude, laser printing has been successfully applied to obtain organic devices exhibiting similar, or even superior, performances as compared to those obtained through conventional techniques. The technique allows for the downsizing of both pixel size and resolution. The simplicity of the procedure stems from its potential to transfer multilayer stacks of solid materials in a single step, without the need of subsequent thermal treatments. On the other hand, solid-state laser printing can lead to the formation of debris on the receiver and is not always easy to integrate in current industrial manufacturing production chains for organic electronic devices.

### 13.3 LIFT in Industry

For the past decade, LIFT technology has contributed to the direct writing of various materials, from simple metals to complex oxides and liquid-phase materials like biological compounds and living cells. LIFT and its modifications could be the technology that is used to create patterns with a feature size ranging from a few micrometres up to few millimetres which can ultimately be implemented into complex microscale structures. Unlike photolithography, LIFT doesn't require to be combined with special optics or other fabrication processes, like etching, being therefore well suited for transfer to industry.

Currently, in addition to the few patents that exist on LIFT, there are also a few companies which use LIFT and different variations of LIFT, adapted to the specific applications envisioned.

In this section, we will present some of the patents that exist on LIFT together with a couple of examples where LIFT has taken the next step forward and made it to industry.

The first patent on a technique used to transfer inks with a laser beam, named laser thermal printing, was submitted in 1993 [65]. The laser is absorbed in a heat-converting layer, and the ink is ejected due to the heat expansion. With this process, digital printing of images with high resolution can be achieved. The process got further developed and patented such that transfers from donor ribbons can be achieved [66,67].

Kodak improved the process further getting the capability of a roll-to-roll printing process where four-colour printing is possible in consecutive production steps [68]. Aurentum GmbH, which was taken over by LPKF Laser and Electronics AG in March 2015, has worked on the development (and obtained a patent) of a laser-based method for digital printing of viscous pastes [69–71].

Furthermore, Daetwyler Graphics AG from Switzerland has built a LIFT prototype for writing inks onto different substrates with a CW pulse-modulated laser working at 1070 nm wavelength [72]. The main idea is to develop a cheap alternative for small-scale rotogravure, i.e. for the production of individual packaging. They can achieve a printing speed of  $5\ \text{m s}^{-1}$  on for 1.2-m-wide foils. The operating principle of the LIFT prototype is based on a laser beam which passes through a transparent substrate and heats up the ink. The solvent vaporizes and the ink is transferred onto a substrate in proximity. In case of transparent inks, the donor substrate is coated with an absorbing layer. The laser light passes through the ink from the front and is absorbed in the layer below on the printing cylinder. The energy of the light is converted to heat and the solvent in the ink on top of it is vaporized leading to an ejection and a transfer.

Based on the same patents, the German company BASF has developed LTP technology [73] to write electrical connections on solar cells by using metal inks. In LTP, the transparent donor, named belt, is coated with the ink in a continuous process using an inking station. The substrate and the guide roll substrate are moved parallel with respect to the laser beam. The donor is moved circularly, and therefore, the unused ink can be recycled as the ink station controls the viscosity of the ink and can replace evaporated solvent if necessary.

This process already fulfils the main requirements for the commercial market as it has a similar speed to screen printing and it is contact-free, digital, and can achieve a line width of  $\leq 60\ \mu\text{m}$ . The ink contains silver or aluminium powders which are already well established in photovoltaic industry, and the printing process is capable with continuous wafer transportation.

Another process similar to LIFT, named LITI (laser-induced thermal imaging), has been patented by Samsung, and it is used for OLED fabrication [74]. In LITI, a light-to-heat conversion layer is used, which absorbs the infrared light, thus heating up the exposed area. This leads in turn to the delamination of the material from the donor which is pressed towards the close-contact receiver substrate. The three different colours for an OLED display are sub-sequentially transferred [75,76]. To overcome the possible damage of the OLEDs due to the separation of the donor and receiver – e.g. device degradation and



the release of gases (e.g. O<sub>2</sub>, H<sub>2</sub>O etc.) from a polyimide film donor – Sony has developed an improved version named laser-induced pattern-wise sublimation (LIPS) [77,78]. In their process, the polymer foil is replaced with a rigid glass substrate, which is easier to align and use. The glass substrate is transferred into vacuum, and the deposition of different layers (hole injection layer, hole transport layer, and bottom electrodes) can be carried out by conventional evaporation. The donor substrate holding the emission layer is placed on top of it holding a small gap. Special clamping equipment holds up the gap in atmospheric pressure where the laser transfer takes place. The patterning of the individual pixel is carried out separately for each emission layer by the process. Other common layers such as an electron transport layer and a top electrode are formed on the patterned substrate after removing the donor glass in inert gas. In contrast to LITI, polymer transfer by LIPS is not possible.

### 13.4 Conclusions and Future Directions

In this chapter, we have reviewed the state of the art and applications of laser-based direct write techniques, in particular LIFT. LIFT, although a relatively new technology, as compared to conventional microfabrication techniques, such as lithography, has contributed to the advancement in the direct printing and patterning industry as well as the success of commercial ink printed for the graphics industry.

For the past 10 years, LIFT has come a long way, from printing different materials, from solids to liquids and customized inks, to their integration into devices, e.g. OLEDs, OTFTs, DNA and protein microarrays, and sensor devices. Modifications to LIFT have been extensively developed for specific applications: blister actuated LIFT for a wide range of bioapplications, LIFT with a metallic interlayer for bioelectronics, biosensors, and gas sensors, reactive LIFT for functional metal oxide semiconductor gas sensors. However, the amount of real sensors printed to this point is still low, and printing sensors is a time-consuming task and improvements of the process are absolutely essential.

Among them, triazene polymers have sturdily emerged as it is able to circumvent the issues in conventional LIFT technology, thereby allowing a high-throughput and high-resolution method with a relatively low cost. This emerging discipline provides alternative routes to overcome current technical barriers in many areas, including electronics, medicine, electromechanical systems, and biosensors. Such a dramatic advancement in science and technology is leading to technology revolutions in a broad range from the next-generation electronic devices to healthcare systems, from cosmetics to textiles, and from agriculture to high-tech businesses.

Up to this point only small amounts of sensors could be printed and the sensors have to be placed individually onto supporting substrates. The sensor microstructures are produced in wafer scale, and it would be desirable to coat the sensors directly on the wafer. Thus, large amounts of samples could be produced leading to a reduced amount of handling. This would in turn reduce the production time as well as the failures due to handling errors.

Moving towards large-scale production a set-up only for LIFT printing of sensors needs to be built. Printing under better controllable conditions is then possible, and faster production can be achieved with improved equipment and without the time required for set-up changes. Ideas about such a prototype were developed within the European e-LIFT project, and possible costs are in the range of 800 000 Euro.

### Acknowledgements

Financial support from the Paul Scherrer Institute, the Romanian National Program 4N/2016, the Commission for Technology and Innovation CTI (Project No. 16713.1 PFNM-NM), and the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, Project Number PN-II-RU-TE-2014-4-2311 (Flex-SENS) is gratefully acknowledged.

### REFERENCES

1. Pimpin A. and Srituravanich W. 2012 Review on micro- and nanolithography techniques and their applications, *Eng. J.* **16** (1) 37–55
2. Gates B. D., Xu Q., Stewart M., Ryan D., Willson C. G. and Whitesides G. M. 2005, New approaches to nanofabrication: Molding, printing, and other techniques, *Chem. Rev.* **105** 1171–96.
3. Chou S. Y., Krauss P. R. and Renstrom P. J. 1996 Imprint lithography with 25-nanometer resolution, *Science* **272** 85–87.
4. Grigorescu A. E. and Hagen C. W. 2009 Resists for sub-20-nm electron beam lithography with a focus on HSQ: state of the art, *Nanotechnol.* **20** 292001.
5. Tseng A. A. 2004 Recent developments in micromilling using focused ion beam technology, *J. Micromech. Microeng.* **14** R15–R34.
6. Shim W., Braunschweig A. B., Liao X., Chai J., Lim J. K., Zheng G. F. and Mirkin C. A. 2011 Hard-tip, soft-spring lithography, *Nature* **469** 516–520.
7. Arnold C., Serra P. and Pique A. 2007 Laser direct-write techniques for printing of complex materials, *MRS Bull.* **32** 23–31.
8. Rothschild M. 2005 Projection optical lithography, *Mater. Today* **8** 18–24.
9. Kumar A. and Whitesides G. M. 1993 Features of gold having micrometer to centimeter dimensions can be formed through a combination of stamping with an elastomeric stamp and an alkanethiol ink followed by chemical etching, *Appl. Phys. Lett.* **63** 2002–2004.
10. Xia Y. et al. 1997 Replica molding using polymeric materials: A practical step toward nanomanufacturing. *Adv. Mater.* **9** 147–149.
11. Zhao X. M., Xia Y. and Whitesides G. M. 1996 Fabrication of three-dimensional microstructures: Microtransfer molding, *Adv. Mater.* **8** 837–840.
12. Jeon S. et al. 2004 Three-dimensional nanofabrication with rubber stamps and conformable photomasks, *Adv. Mater.* **16** 1369–1371.

13. Schiff H. 2015 Nanoimprint lithography: 2D or not 2D? A review, *Appl. Phys. A* **121** 415–435.
14. Garcia R., Knoll A. W. and Riedo E. 2014 Advanced scanning probe lithography, *Nature Nanotechnology* **9** 577–587.
15. Rosi N. L. and Mirkin C. A. 2005 Nanostructures in Biodiagnostics, *Chem. Rev.* **105** (4) 1547–1562.
16. Kopitkovas G., Lippert T., David C., Sulcas R., Hobley J., Wokaun A., and Gobrecht J. 2004 Laser micromachining of optical devices, *Proc. SPIE* **5662** 515.
17. Braudy R. S. 1969 Laser writing, *Proc. IEEE* **57** (10) 1771–1772.
18. Levene M. L., Scott R. D. and Siry B. W. 1970 Material transfer recording, *Appl. Opt.* **9** (10) 2260–2265.
19. Bohandy J., Kim B. F. and Adrian F. J. 1986 Metal deposition from a supported metal film using an excimer laser, *J. Appl. Phys.* **60** (4) 1538–1539.
20. Greer J. A. and Parker T. E. 1988 Laser induced forward transfer of metal oxides to trim the frequency of surface acoustic wave resonator devices, *Proc. SPIE* **998** 113–125.
21. Kattamis N. T., Brown M. S., Arnold C. B. 2011 Finite element analysis of blister formation in laser-induced forward transfer, *J. Mater. Res.* **26** (18) 2438–2449.
22. Nagel M., Hany R., Lippert T., Molberg M., Nuesch F. A. and Rentsch D. 2007 Aryltriazene photopolymers for UV-laser applications: Improved synthesis and photodecomposition study, *Macromol. Chem. Phys.* **208** (3) 277–286.
23. Hopp B., Smausz T., Barna N., Vass C., Antal Z., Kredics L. and Chrisey D. B. (2005) Time-resolved study of absorbing film assisted laser induced forward transfer of *Trichoderma longibrachiatum* conidia, *J. Phys. D: Appl. Phys.* **38** 833–837.
24. Tolbert W. A., Sandy Lee I. Y., Doxtader M. M., Ellis E. W. and Dlott D. D. 1993 High-speed color imaging by laser ablation transfer with a dynamic release layer: fundamental mechanisms, *J. Imaging Sci. Technol.* **37** 411–421.
25. Lee S. T., Lee J. Y., Kim M. H., Suh M. C., Kang T. M., Choi Y. J., Park J. Y., Kwon J. H., Chung H. K., Baetzold J., Bellmann E., Savvateev V., Wolk M. and Webster S. 2002 A new patterning method for full-color polymer light-emitting devices: Laser induced thermal imaging (LITI), *SID Symp. Dig. Tech. Pap.* **33**(1) 784–787.
26. Palla Papavlu A. and Lippert T. (2017) Chapter 3: LIFT with a dynamic release layer. In *Laser Printing of Functional Materials: Electronics, 3D Microfabrication and Biomedicine* First Edition, A. Pique and P. Serra (eds.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
27. Lippert T. 2009 UV Laser ablation of polymers: From structuring to thin film deposition. In *Laser-Surface Interactions for New Materials Production Tailoring Structure and Properties*, A. Miotello, P. M. Ossi (eds.), Springer Series in Materials Chemistry Vol. 130, Springer, Berlin, pp. 141–175.
28. Dinca V., Palla-Papavlu A., Dinescu M., Shaw-Stewart J., Lippert T., Di Pietrantonio F., Cannata D., Benetti M. and Verona E. 2010 Polymer pixel enhancement by laser-induced forward transfer for sensor applications, *Appl. Phys. A* **101**(3) 559–565.
29. Palla-Papavlu A., Paraico I., Shaw-Stewart J., Dinca V., Savopol T., Kovacs E., Lippert T., Wokaun A. and Dinescu M. 2011 Liposome micropatterning based on laser induced forward transfer, *Appl. Phys. A* **102**(3) 651–659.
30. Doraiswamy A., Narayan R., Lippert T., Urech L., Wokaun A., Nagel M., Hopp B., Dinescu M., Modi R., Auyeung R. and Chrisey D. 2006 Excimer laser forward transfer of mammalian cells using a novel triazene absorbing layer, *Appl. Surf. Sci.* **252** 4743–4747.
31. Fardel R., Nagel M., Nuesch F., Lippert T. and Wokaun A. 2007 Fabrication of organic light-emitting diode pixels by laser-assisted forward transfer, *Appl. Phys. Lett.* **91** 061103.
32. Mattle T., Hintennach A., Lippert T. and Wokaun A. 2013 Laser induced forward transfer of SnO<sub>2</sub> for sensing applications using different precursors systems, *Appl. Phys. A* **110** 309–316.
33. Palla Papavlu A., Mattle T., Temmel S., Lehmann U., Hintennach A., Grisel A., Wokaun A. and Lippert T. 2016 Highly sensitive SnO<sub>2</sub> sensor via reactive laser-induced transfer, *Sci. Rep.* **6** 25144.
34. Boutoupoulos C., Touloupakis E., Pezzotti I., Giardi M. T. and Zergioti I. 2011 Direct laser immobilization of photosynthetic material on screen printed electrodes for amperometric biosensor, *Appl. Phys. Lett.* **98**(9) 093703-1–093703-3.
35. Dinca V., Ranella A., Farsari M., Kafetzopoulos D., Dinescu M., Popescu A. and Fotakis C. 2008 Quantification of the activity of biomolecules in microarrays obtained by direct laser transfer, *Biomed. Microdevices* **10**(5) 719–25.
36. Fernandez-Pradas J. M., Colina M., Serra P., Dominguez J. and Morenza J. L. 2004 Laser-induced forward transfer of biomolecules, *Thin Solid Films* **453–454** 27–30.
37. Karaiskou A., Zergioti I., Fotakis C., Kapsetaki M. and Kafetzopoulos D. 2003 Micro fabrication of biomaterials by the sub-ps laser-induced forward transfer process, *Appl. Surf. Sci.* **208** 245–249.
38. Chrisey D., Pique A., McGill R., Horwitz J., Ringeisen B., Bubb D. and Wu P. 2003 Laser deposition of polymer and biomaterial films, *Chem. Rev.* **103** 553–576.
39. Duocastella M., Fernandez-Pradas J., Dominguez J., Serra P. and Morenza J. 2008 Printing biological solutions through laser-induced forward transfer, *Appl. Phys. A* **93**(4) 941–945.
40. Duocastella M., Fernandez-Pradas J. M., Morenza J. and Serra P. 2009 Time-resolved imaging of the laser forward transfer of liquids, *J. Appl. Phys.* **106**(8) 084907-1–084907-7.
41. Patrascioiu A., Duocastella M., Fernández-Pradas J. M., Morenza J. L. and Serra P. 2011 Liquids microprinting through a novel film-free femtosecond laser based technique, *Appl. Surf. Sci.* **257** 5190–5194.
42. Eason R. (ed.) 2006 *Pulsed Laser Deposition of Thin Films: Applications – LED Growth of Functional Materials*. Wiley. ISBN: 978-0-471-44709-2.
43. Palla Papavlu A., Dinca V., Filipescu M. and Dinescu M. 2017 Matrix assisted pulsed laser evaporation of organic thin films: Applications in biology and chemical sensors. In *Laser Ablation – From Science to Applications*, T. E. Itina (ed.), Intech. ISBN 978-953-51-5565-2.
44. Ringeisen B. R., Chrisey D. B., Pique A., Young H. D., Modi R., Bucaro M., Jones Meehan J. and Spargo B. J. 2002 Generation of mesoscopic patterns of viable *Escherichia coli* by ambient laser transfer, *Biomaterials* **23** 161.
45. Piqué A., Auyeung R. C. Y., Metkus K. M., Kim H., Mathews S. A., Bailey T., Chen X. and Young L. J. 2008 Laser decal transfer of electronic materials with thin film characteristics, *Proc. SPIE* 6879, 687911-1–687911-8.

46. Auyeung R. C. Y., Kim H., Birnbaum A. J., Zalalutdinov M. K., Mathews S. A. and Piqué A. 2009 Laser decal transfer of freestanding microcantilevers and microbridges, *Appl. Phys. A* **97** 513519.
47. Birnbaum A. J., Auyeung R. C. Y., Wahl K. J., Zalalutdinov M. K., Laracuente A. R. and Piqué A. 2010 Laser printed micron-scale free standing laminate composites: Process and properties, *J. Appl. Phys.* **108** 83526-1–83526-7.
48. Puerto D., Biver E., Alloncle A. P. and Delaporte P. 2016 Single step high-printing of continuous silver lines by laser-induced forward transfer, *Appl. Surf. Sci.* **374** 183–189.
49. Wang J., Auyeung R. C. Y., Kim H., Charipar N. A. and Piqué A. 2010 Three-dimensional printing of interconnects by laser direct-write of silver nanopastes, *Adv. Mater.* **22** 4462.
50. Palla-Papavlu A., Dinca V., Paraico I., Moldovan A., Shaw-Stewart J., Schneider C. W., Kovacs E., Lippert T. and Dinescu M. 2010 Microfabrication of polystyrene micro-bead arrays by laser induced forward transfer, *J. Appl. Phys.* **108** 033111-1–033111-6.
51. Palla Papavlu A., Dinca V., Luculescu C., Shaw-Stewart J., Nagel M. and Dinescu M. 2010 Laser induced forward transfer of soft materials, *J. Opt.* **12** 124114-1–124114-9.
52. Palla-Papavlu A., Córdoba C., Patrascioiu A., Fernández-Pradas J. M., Morenza J. L. and Serra P 2013 Deposition and characterization of lines printed through laser-induced forward transfer, *Appl. Phys. A* **110** 751.
53. Kim H., Auyeung R. C. Y., Lee S. H., Huston A. L. and Piqué A. 2009 Laser forward transfer of silver electrodes for organic thin-film transistors, *Appl. Phys. A* **96** 441–445.
54. Boutopoulos C., Kalpyris I., Serpetzoglou E. and Zergioti I. 2014 Laser-induced forward transfer of silver nanoparticle ink: time-resolved imaging of the jetting dynamics and correlation with the printing quality, *Microfluid. Nanofluid.* **16** (3) 493–500.
55. Biver E., Rapp L., Alloncle A. P., Serra P. and Delaporte P. 2014 High-speed multi-jets printing using laser forward transfer: Time-resolved study of the ejection dynamics, *Opt. Express* **22** (14) 17122–17134.
56. Delaporte P. and Alloncle A. P. 2016 Laser-induced forward transfer: A high resolution additive manufacturing technology, *Opt. Laser Technol.* **78** 33–41.
57. Rapp L., Biver E., Alloncle A. P. and Delaporte P. 2014 High-speed laser printing of silver nanoparticles ink, *J. Laser MicroNanoEng.* **9** (1) 5–9.
58. Cannatà D., Benetti M., Di Pietrantonio F., Verona E., Palla-Papavlu A., Dinca V., Dinescu M. and Lippert T. 2012 Nerve agent simulatant detection by solidly mounted resonators (SMRs) polymer coated using laser induced forward transfer (LIFT) technique, *Sens. Actuators B* **173** 32–39.
59. Di Pietrantonio F., Benetti M., Cannatà D., Verona E., Palla-Papavlu A., Dinca V., Dinescu M., Mattle T. and Lippert T. 2012 Volatile toxic compound detection by surface acoustic wave sensor array coated with chemoselective polymers deposited by laser induced forward transfer: Application to sarin, *Sens. Actuators B* **174** 158–167.
60. Touloupakis E., Boutopoulos C., Buonasera K., Zergioti I. and Giardi M. T. 2012 A photosynthetic biosensor with enhanced electron transfer generation realized by laser printing technology, *Anal. Bioanal. Chem.* **402** (10) 3237–3244.
61. Palla-Papavlu A., Patrascioiu A., Di Pietrantonio F., Fernández-Pradas J. M., Cannatà D., Benetti M., D'Auria S., Verona E. and Serra P. 2014 Preparation of surface acoustic wave odor sensors by laser-induced forward transfer, *Sens. Actuators B* **192** 369–377.
62. Di Pietrantonio F., Benetti M., Cannatà D., Verona E., Palla-Papavlu A., Fernández-Pradas J. M., Serra P., Staiano M., Varriale A. and D'Auria S. 2015 A surface acoustic wave bio-electronic nose for detection of volatile odorant molecules, *Biosens. Bioelectron.* **67** 516–523.
63. Shaw-Stewart J., Mattle T., Lippert T., Nagel M., Nuesch F. A. and Wokaun A. 2013 The fabrication of small molecule organic light-emitting diode pixels by laser-induced forward transfer, *J. Appl. Phys.* **113** 043104.
64. Kattamis N. T., McDaniel N. D., Bernhard S. and Arnold C. B. 2011 Ambient laser direct-write printing of a patterned organo-metallic electroluminescent device, *Org. Electron.* **12** 1152–1158.
65. Kaneko A., Hitomi C. and Hoshikawa J. 1993 Laser printer and thermal transfer printing method. European Patent EP0542544.
66. Hutt K. W., Hann R. A. and Tran H. C. V. 1999 Laser dye thermal transfer printing, United State Patent 5864356
67. Chang S. 2002 Transfer printing, United State Patent 6476842.
68. Moulin M. and Huang J. 2005 Method and apparatus for laser-induced thermal transfer printing, United State Patent 6894713.
69. Lehmann U. and Meyer D. 2009 Quality printing method and printing machine, European Patent EP1485255
70. Lehmann U. 2011 Printing machine and printing method therefore, European Patent EP2155499.
71. Lehmann U. 2007 Method of printing and corresponding print machine, European Patent EP1268211.
72. Hennig G., Baldermann T., Nussbaum C., Rossier M., Brockelt A., Schuler L. and Hochstein G. 2012 Lasersonic lift process for large area digital printing, *J. Laser Micro/Nanoeng.* **7** (3) 299–305.
73. Jager F. K., Kaczun J. and Lehmann U. 2011 Printing machine and methode for printing a substrate, United State Patent 20110310205.
74. Sun J. W., Kang T. M., Noh S. W. and Suh M. C. 2012 Laser induced thermal imaging mask, laser irradiation apparatus including the same, and method of manufacturing organic light emitting device by using the same, United State Patent 20120099615.
75. Wolk M., Potts J., Li Y. and Huynh K. 2010 Donor films with pattern-directing layers, United State Patent 12/557675.
76. Wolk M. B., Lamansky S. and Tolbert W. A. 2008 Progress in laser induced thermal imaging of oleds, *SID Symp. Dig. Tech. Pap.* **39**(1) 511–514.
77. Hirano T., Matsuo K., Kohinata K., Hanawa K., Matsumi T., Matsuda E., Matsuura R., Ishibashi T., Yoshida A and Sasaoka T 2007 53.2: Distinguished paper: Novel laser transfer technology for manufacturing large-sized oled displays, *SID Symp. Dige. Tech. Pap.* **38**(1) 1592–1595.
78. Blanchet G. B., Loo Y.-L., Rogers J., Gao F. and Fincher C. 2003 Large area printing of organic transistors via a high throughput dry process. In Materials Research Society Symposium Proceedings, vol. 736. Cambridge Univ Press, 283–288.