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Laser-induced forward transfer: propelling liquids with light

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Abstract

Laser-induced forward transfer (LIFT) constitutes an interesting alternative to conventional printing techniques in microfabrication applications. Originally developed to print inorganic materials from solid films, it was later proved that LIFT was feasible for printing liquids as well, which substantially broadened the range of printable materials. Any material which can be suspended or dissolved in an ink can be in principle printed through LIFT.

The principle of operation of LIFT relies on the localized absorption of a focused laser pulse in a thin film of the ink containing the material to print (donor). This results in the generation of a cavitation bubble which expansion displaces a fraction of the liquid around it, leading to the formation of a jet which propagates away the donor and towards the receiving substrate, placed at a short distance from the liquid free surface. The contact of the jet with this receiving substrate results in the deposition of a sessile droplet. Thus, each droplet results from a single laser pulse, and the generation of micropatterns is achieved through the printing of successive droplets. A similar ejection and deposition process is produced by generating a cavitation bubble below the surface of a liquid contained in a reservoir in the film-free laser printing configuration.

In this work we review our main achievements on the laser printing of inks, paying special attention to the analysis of the liquid transfer dynamics and its correlation with the printing outcomes.

Keywords: Laser-induced forward transfer; film-free laser printing; liquid printing

1. Introduction

Engraving and printing symbols or text gave rise to perdurable memory of human history. For many centuries printing techniques were devised for writing and graphic arts purposes with the goal to spread culture and knowledge. By now, the printing of materials has been extended to other industrial areas for marking, labeling and as a new approach for the fabrication of devices, like in the ever growing field of printed electronics, for example. This extension required the invention of new methods to transfer materials and the design of new inks adapted to these methods. Traditional techniques such as screen-printing, photolithography or stamp based methods require the use of masks or moulds. However, these traditional methods, with good performance in mass production, lack the flexibility required for rapid-prototyping and for the manufacture of customized products on demand, and are not well suited to satisfy the needs of rapidly changing markets. On the contrary, direct-write techniques, being maskless and allowing printing sequentially, make possible the fast transfer from design to production, which makes them perfectly suited for digital manufacturing. Hence, inkjet, dip-pen, or laser-based printing techniques can easily transfer patterns that can be different in every printing process, and therefore facilitate the transition from the digital file to the end product [1].

Many direct-write techniques rely on the transfer of droplets with resolutions in the micrometers range in order to create patterns of metals, semiconductors, polymers, and even biological materials such as DNA, protein or cells [1]. Thus, these techniques can be applied in a quite straightforward way to the production of electronic devices, sensors, biomedical devices, and even for tissue engineering in regenerative medicine applications. Among the direct-write techniques inkjet printing is probably the best-known. It is based on thermoelectric or piezoelectric actuators that promote the expulsion of a tiny amount of liquid through a nozzle [2-4] whose dimensions limit the minimum size of the droplets that can be dispensed and the maximum size of the suspended particles permissible in the ink. Hence, the decrease of the droplet size requires smaller nozzles which are in turn more prone to clogging. Dip-pen microspotting is also a well-established technique based on the actuation of capillary forces to transfer inks from a sharp tip onto a substrate, being mostly used for the printing of biological materials and the production of microarrays. With its resolution determined by the tip size, sub-micron resolutions can be reached through especially adapted AFM-tips, but at highly punishing processing speeds [5].

More recently, laser-induced forward transfer (LIFT) was suggested as an interesting alternative for the printing of materials from liquid suspensions or pastes [6]. The principle of operation is the same as the one for the LIFT from solid donor films [7, 8], a process that was first described in the late sixties [9, 10]. The material is transferred from a donor thin film previously deposited on a substrate which is transparent to the laser radiation. The action of a laser pulse focused through the donor substrate in the interface between this substrate and the thin donor film promotes the ejection of material towards the receiver substrate. One of the main advantages of LIFT is that it does not require a nozzle, avoiding the characteristic clogging problems of inkjet printing. Additionally, it is not too restrictive with the rheological properties and viscosities of the inks that can be printed, thus enlarging the list of printable materials and simplifying the formulation of new specific inks. When the ink is transparent to the laser radiation printing can also be carried out from the liquid directly contained in a reservoir through the use of ultrashort laser pulses, hence skipping the step of producing the donor film [11]. This technique, based in the same principle as LIFT, is known as film-free laser printing [12].

In this brief review we present an overview of the different laser printing techniques outlined above, with special emphasis on the mechanisms which make possible to use laser light to propel liquids with the aim of depositing inks for the fabrication of miniaturized devices.

2. Experimental setup

A sketch of the principle of operation of LIFT is presented in Figure 1a. The most common is to use a laser source delivering short (ns) or ultrashort (ps or fs) pulses, with its wavelength in accordance with the donor substrate and ink properties. In general, glass is used as donor substrate with near-infrared and visible laser wavelengths, while quartz or fused silica substrates are typically used for UV wavelengths. However, other materials are possible as well (like flexible organic substrates in roll-to-roll production), as long as they are transparent to the laser radiation. On the contrary, the ink must absorb the laser radiation to be transferred. However, this requirement can be skipped by using an absorbing layer between the donor substrate and the liquid [13, 14]. This layer is usually a metallic thin film of some tens of nanometers or a thicker polymeric layer (up to a few microns), that in some cases decomposes during transfer. Typically, few microjoules per pulse are needed for printing micron-sized droplets of water-based solutions with metallic absorbing layers or common inkjet printing conductive inks [13, 15-21]. However, the pulse energies required for printing depend in general on the size of the laser beam on the donor film , the specific properties of the donor system and the characteristics of the droplets that have to be printed. The laser repetition rate, in turn, is related with the speed at which the printing process is performed.

The laser beam in a laser printing setup is usually guided through mirrors and beam-splitters up to a converging lens that focuses the radiation onto the interface between the donor substrate and the ink or at the absorbing layer, if present. The donor system consists of a solid substrate transparent to the laser radiation and the liquid layer of ink that has been spread on its surface, with a thickness commonly ranging from a few microns up to around 100 μm. If required, the absorbing layer must be previously deposited. The receiving substrate is placed in front and parallel to the donor liquid surface, and the gap between them is not usually a restrictive parameter: it can range from a few tens of micrometers up to few millimeters, depending on the operating conditions, a degree of tolerance which constitutes a real advantage in terms of further industrial implementation.

A motion stage system able to translate the donor/receiving substrates with respect to the laser beam is needed to generate patterns. Alternatively, the laser beam can be scanned along the donor layer by means of galvanometric mirrors or other beam deflection devices. The patterns are generated by sequentially printing droplets, in a very similar way to most digital printing techniques. The printing process can be usually performed at ambient conditions (vacuum is not a requirement), though if necessary for the production of extremely delicate devices it is also compatible with clean-room facilities.

In the case of film-free laser printing the deposition setup is not essentially different from that of LIFT, except that the ink is contained in a reservoir and it must be transparent to the laser radiation (Figure 1b). Additionally, ultrashort laser pulses (fs or ps) are required in order to promote absorption of the laser pulse energy in the liquid through non-linear mechanisms [22]. With the focal point conveniently located a few microns below the free surface of the liquid transfer is possible and it leads to an identical outcome to that of LIFT [23, 24].

3. Mechanisms of liquid ejection and deposition

Time-resolved imaging studies of the printing process helped to understand the underlying mechanisms of LIFT [25-34]. The process of printing droplets starts with the absorption of the laser pulse energy on the donor system. Figure 2 shows a series of time-resolved images of a typical liquid ejection event leading to the further deposition of liquid on a substrate and resulting in dome-shaped and reproducible droplets [28]. As a result of the energy absorption a vapor bubble is generated in the liquid film. The high pressure of the gas produces the expansion of the bubble pushing the liquid around it (see sketch in figure 3). This generates a pressure gradient between the bubble sides and its pole that promotes liquid flow to the pole along the bubble walls. The convergence of liquid at the pole of the bubble from the sides produces an increase of the pressure at that point which is released through the formation of a very thin needle-like jet. In spite of the further bubble collapse, the jet continues advancing towards the receiving substrate, usually at speeds that range from some tens to few hundreds of meters per second [26], depending on the laser fluence. The so formed jets are perfectly stable and have a high-aspect ratio, with lengths that can easily reach a few millimeters before breaking [25]. This permits the tolerance in the gap between donor and receiving substrates previously mentioned that facilitates the implementation of LIFT in existing production lines and makes it easily compatible with roll-to-roll fabrication processes. Despite the high-speed of the jet, the deposition process and droplet formation is normally gentle enough to avoid splashing issues [35]. After the landing of the jet tip onto the receiving surface, the liquid spreads in a similar way as a drop impacting on a dry surface at moderate speed [35]. After a very few microseconds the spreading stops while the jet continues to feed the growing droplet in a process that presents significant similarities with that of adding liquid to a sessile drop [36]. At this stage the continuous feeding of liquid from the jet promotes an increase of the volume and the contact angle of the droplet until finally, after a few hundreds of microseconds, the jet breaks due to the onset of Plateau-Rayleigh instabilities [37]. At this moment, liquid feeding is completely stopped and the droplet starts a slow relaxation process diminishing the contact angle and increasing its diameter up to its final dimensions.

At laser fluences just below the threshold for material transfer, time-resolved imaging has revealed that the jet is also formed, but in this case it recoils after the bubble collapse and before reaching the receiving substrate (obviously, the threshold depends on the gap between donor and receiving substrates). On the other hand, too high laser fluences generate pressures inside the bubble high enough to overcome surface tension, which leads to the burst of the liquid wall around the bubble and the consequent splashing of the liquid collected by the receiving substrate [26].

Though we have so far described the typical liquid transfer scenario in the LIFT of liquids, the printing mechanisms may differ from those stated above depending on the working conditions. Indeed, when the gap between the liquid film and the receiving substrate is smaller than the maximum height of the bubble, this contacts the receiving surface before the jet can be developed during free flight [38, 39]. After the impact, the bubble collapses from its end and is progressively transformed into a jet while in contact with the surface. Anyway, dome-shaped and uniform droplets can also be printed under this transfer process; actually this alternative mechanism has been very recently revealed effective for the fabrication of high quality microlenses through LIFT [40]. Slight differences also appear in the mechanism of jet formation when the thickness of the liquid film is substantially smaller than the dimensions of the laser spot [29]. In this case, the radial expansion of the bubble along the solid surface plane is small and, consequently, the gradient of pressure responsible for liquid accumulation on the pole of the bubble is too low to generate the needle-like jet described above. Nevertheless, a jet is generated as well, this time as a result of bubble collapse from its sides while the liquid front continues advancing in the axial direction; this, however, presents a substantially smaller aspect ratio than in the former case. Once formed, the jet is stable and continues advancing towards the receiving substrate.

The formation of stable jets is also possible by a blister actuated mechanism promoting only the deformation of the absorbing layer [41, 42]. In this case, the absorbing layer is not completely ablated and the generated vapor remains encapsulated in the interface with the donor substrate. Vapor expansion promotes the deformation of the absorbing layer that transmits its impulsion to the liquid. A jet is then directly generated without the presence of any vapor bubble in the liquid. The jet is developed by the sudden transfer of momentum to the liquid by the generated blister.

Time-resolved imaging studies of the LIFT process with thick donor liquid films (around 100 μm) revealed the emergence of a thicker second jet following the first needle-like jet which originates after a delay of several microseconds [43, 44]. Similar double-jet formation was also observed in film-free laser printing experiments [11, 12]. The special configuration of this last technique, where printing can be performed directly from a reservoir, allows the simultaneous observation of the processes occurring both underneath and above the liquid surface [45, 46]. Figure 4 shows a series of time-resolved images of a film-free laser printing event where bubble and jet dynamics can be simultaneously observed and correlated, something which is practically impossible in a LIFT configuration. The absorption of the laser pulse produces a bubble that rapidly expands. When the bubble reaches the free liquid surface, it pushes a small amount of liquid away from the free surface, generating a jet on the bubble upper pole due to the pressure gradient in the liquid described in the case of LIFT. The bubble is flattened on its upper pole near the surface during bubble collapse, as it can be observed in the image taken after a delay of 16 μs. One microsecond later a second bubble starts to appear from the bottom of the collapsing bubble. The emergence of the second bubble gives us clues about the processes occurring inside the liquid and the evolution of the bubble geometry. The liquid overpressure occurring in the pole due to the flow of liquid from the sides generates the observed outward jet but also an inward counter-jet that propagates in opposite direction, that is, downwards. The counter-jet penetrates the already collapsing bubble transforming it into a torus, and as soon as the counter-jet tip impacts the bottom of the bubble the secondary bubble emerges as a result of that impact. This behavior has been well described through the numerical resolution of the fluid dynamics equations for a high pressure bubble generated close to the free surface of a liquid [47]. The re-expansion of the torus-shaped bubble promotes the formation of the thicker second jet observed in the images. This time, the liquid overpressure is generated on the circular pole of the torus instead of in the single-point pole of the sphere. Consequently, the jet presents a clearly cylindrical shape during the early stages of its expansion instead of the typical needle-like shape observed during LIFT with relatively thin donor films. Later, it evolves by forming a thick jet that accumulates liquid at the tip and progressively thins its central part until it pinches-off.

4. Droplets printing through LIFT

The characteristics of the droplets printed through LIFT mainly depend on the laser parameters, the ink properties and the surface properties of the receiving substrate. The first studies already demonstrated that by using adequate laser parameters uniform droplets with a circular perimeter could be printed with high reproducibility [13, 48, 49], and that the use of absorbing layers allowed the printing of non-absorbing inks and made LIFT independent of the laser wavelength. Furthermore, absorbing layers can enlarge the window of laser pulse energies at which circular droplets can be printed, hence simplifying the adjustment of the laser parameters [20].

The diameter of the droplets and their shape are strongly dependent of the wetting properties of the transferred ink on the receiving substrate [50]. Consequently, correlations between the printing parameters and the amount of transferred liquid can be better inferred from volume measurements. Figure 5 shows the image of an array of a water and glycerol 50% (v/v) solution printed by LIFT at different laser pulse energies. Above a certain threshold there is a considerable range of laser fluences allowing to get circular and uniform droplets [15, 51], whose volume has been found to increase linearly with laser pulse energy/fluence. Values above this range produce droplets with irregular and non reproducible shapes, with small satellites around them, and for even higher values the complete splashing of the droplets. These features can be correlated with the dynamics of the jets [26]. Below the energy threshold for printing, the bubble expansion is not strong enough to make the jet or the liquid protrusion reach the receiving substrate before retraction. Above the threshold, the transfer occurs in a gentle way as described in section 3. However, when the pulse energy is too high, the pressure of the expanding bubble can overcome the surface tension of the liquid and promote burst before the jet is formed.

The thickness of the donor film influences the amount of liquid that is being printed. At fluences clearly above the transfer threshold it is found that the volume of printed liquid is increasing monotonically for a thicker donor film and fixed irradiation conditions [28, 50, 52]. In fact, if the laser spot diameter determined by the fluence threshold is larger than the donor film thickness, the volume of the printed droplet coincides with the volume of liquid delimited by the corresponding laser spot area [15, 29]. In this case, the bubble acts as a piston pushing the liquid in front of it, and the contribution of liquid flow from the bubble sides is negligible, as we have pointed out in Section 3; these are the situations which lead to bubbles with practically no lateral expansion and relatively thick jets. However, when the thickness of the donor film is larger than the laser spot diameter, the bubble expands more isotropically and drags substantial amount of liquid from the sides, which contributes to higher amounts of transferred volume. This is the situation corresponding to the typical needle-like jets described above (Figs. 2 and 4). From all this it is clear that printing very small droplets requires very thin films and fluences close to threshold. Droplet diameters below 10 μm and volumes of few femtoliters have been successfully printed in this way, though it has to be pointed out that under such critical conditions reproducibility is easily compromised: fluctuations in the laser pulse energy or in the donor film thickness can severely alter the printing outcome [51].

Finally, it is worth to state that one of the main advantages of LIFT is that it is possible to print liquids in a wide range of viscosities, ranging from a few mPa·s up to some Pa·s [53, 54]. The volume of droplets printed under similar focusing conditions decreases slightly with increasing viscosity [54]. Liquids with higher viscosity withstand higher internal pressures of the expanding bubble before bursting, and the dissipating role of viscous forces stabilizes the jetting dynamics. Therefore, working with high viscosities makes the printing process more reproducible and less prone to splashing. However, higher laser fluences are required, which is detrimental from an economic point of view.

5. Summary

The printing of liquids with lasers is mediated by the generation of large and stable jets that gently transfer the liquid from a donor thin film in the LIFT configuration, or directly from a reservoir in the film-free laser printing approach. In both cases, the jets are generated after the expansion of a vapor bubble due to the flow of liquid along the bubble walls and that accumulates in the pole. Dome-shaped and uniform droplets can be printed from a wide range of liquid rheologies and viscosities, and the control of the focusing conditions and the laser pulse energy allows tuning the amount of liquid which is finally printed. The smallest droplet size can be obtained by using highly focused laser beams, low pulse energies and very thin donor liquid films. The versatility for printing different kind of materials and ink formulations at high resolution makes us foresee a promising future for LIFT in digital manufacturing.

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Figure captions

Figure 1. Principle of operation of a) the LIFT technique and b) the film-free laser printing technique. *d* in the insert is the distance below the free surface where the focal point is located.

Figure 2. Time resolved images of the dynamics obtained during the LIFT of a water and glycerol solution at different delay times with respect to the arrival of the laser pulse. The corresponding delay time is indicated above each image, and the image exposure time is always 100 ns. In all of the frames, the laser impinges from above. Image below shows deposited droplets on the receiver substrate after transfer. Reprinted from [28] with permission from Elsevier.

Figure 3. Sketch of the initial expansion of the vapor bubble generated after the absorption of laser pulse energy in the LIFT process. Geometric configuration is similar to that shown in Figure 2: the laser beam is focused from above across the donor substrate. The expansion of the vapor bubble generates a pressure gradient between the bubble sides and its pole that promotes a net liquid flow towards the pole from the sides of the bubble.

Figure 4. Time resolved images corresponding to a liquid ejection event generated with the film-free laser printing technique for a water and glycerol solution. In all of the frames, the laser impinges the liquid surface from above, being focused at a depth of around 80 μm below the free-surface, which appears as a bright band approximately at half the height of the images. Adapted from [46] with permission from Elsevier.

Figure 5. Optical microscopy image of an array of droplets of a water and glycerol solution printed on a poly-L-lysine coated glass slide; each row was printed at a

different laser pulse energy. All the columns are printed using the same laser parameters. Adapted from [26] with permission from AIP.

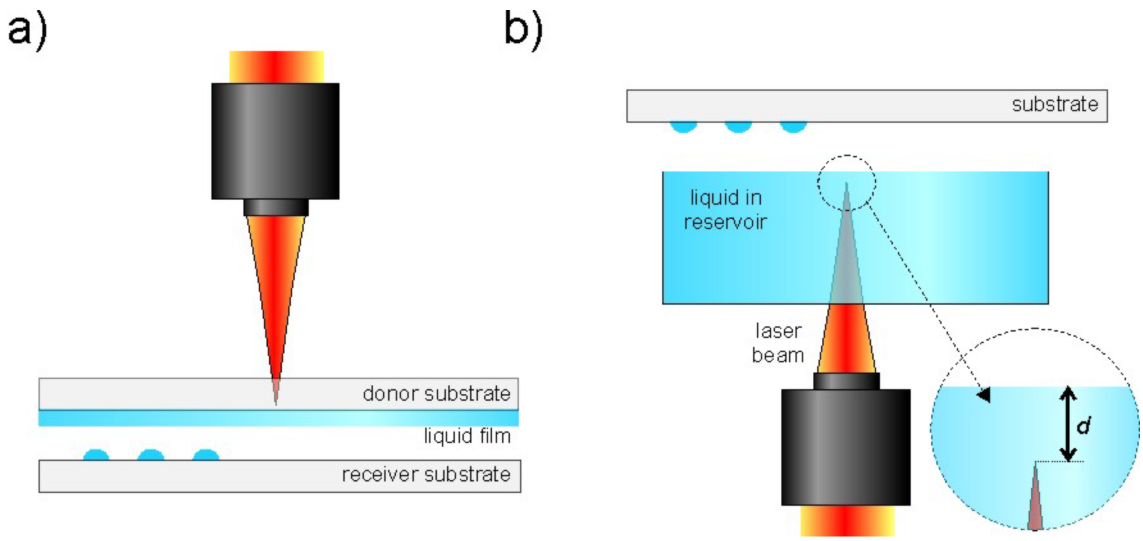
a)
donor substrate
liquid film
receiver substrate
b)
substrate
liquid in reservoir
laser beam
d

Figure 1

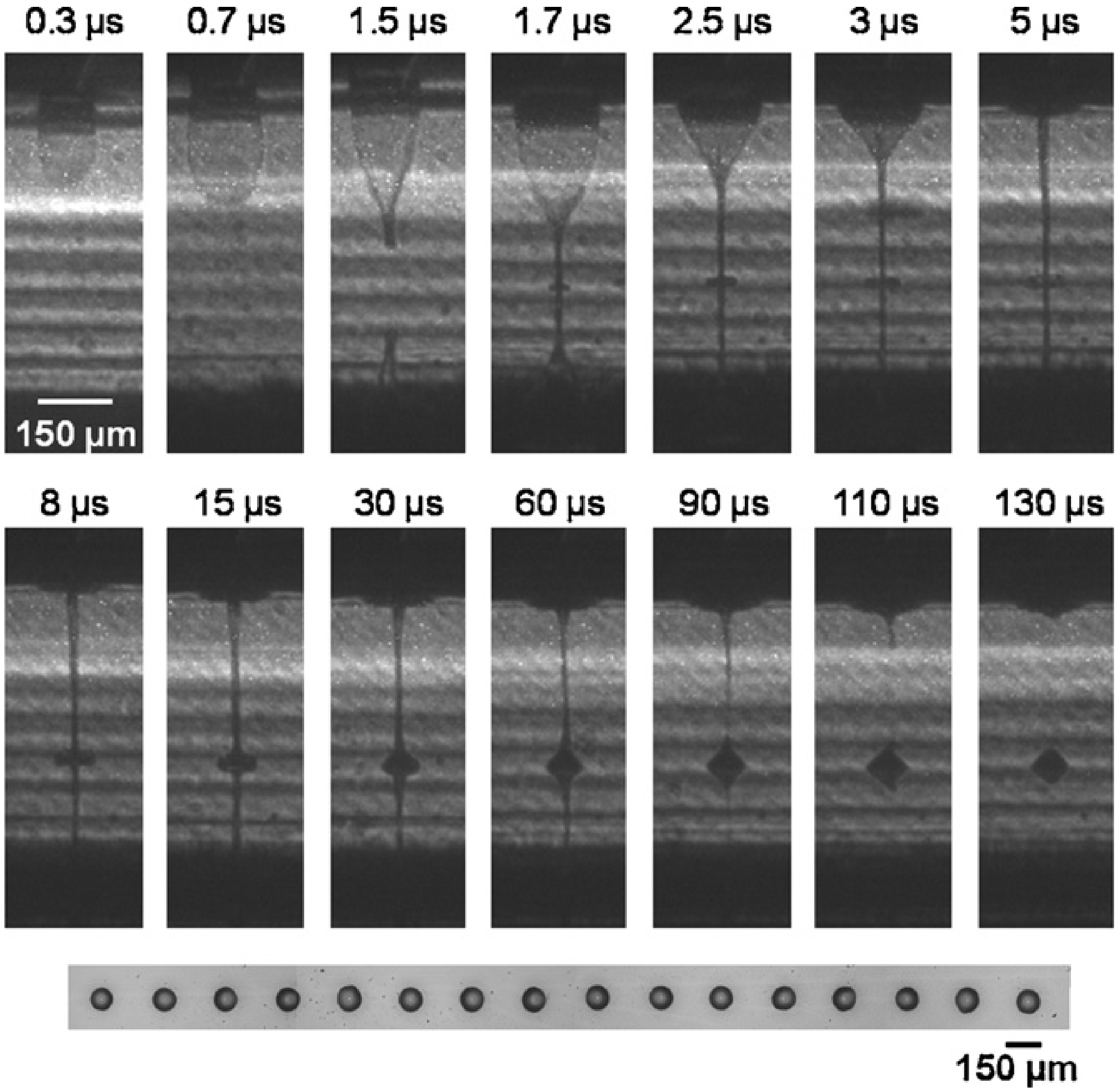
0.3 µs
0.7 µs
1.5 µs
1.7 µs
2.5 µs
3 µs
5 µs
150 µm
8 µs
15 µs
30 µs
60 µs
90 µs
110 µs
130 µs
150 µm

Figure 2

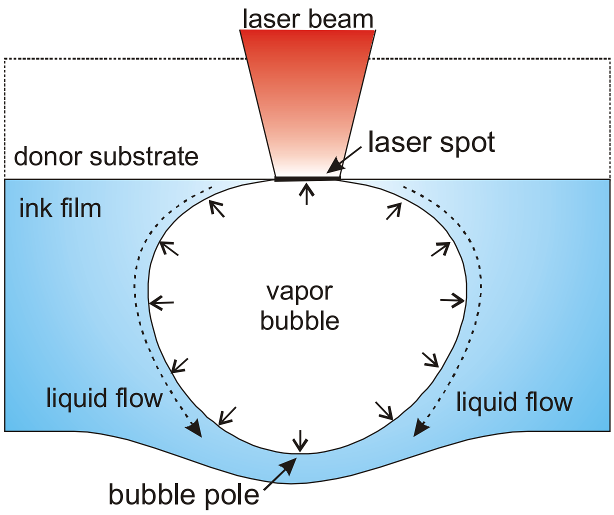
laser beam
laser spot
donor substrate
ink film
vapor
bubble
liquid flow
liquid flow
bubble pole

Figure 3

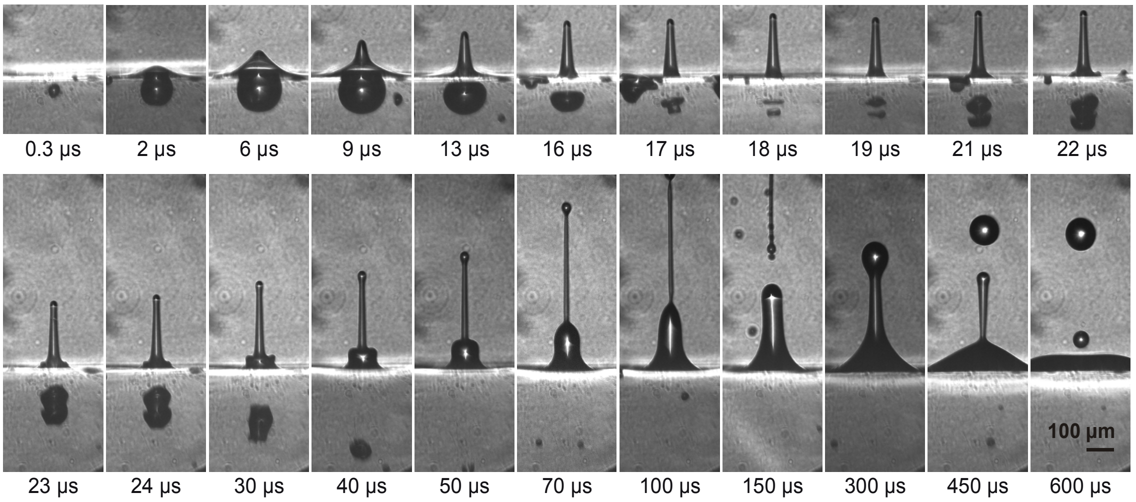
0.3 µs
2 µs
6 µs
9 µs
13 µs
16 µs
17 µs
18 µs
19 µs
21 µs
22 µs
23 µs
24 µs
30 µs
40 µs
50 µs
70 µs
100 µs
150 µs
300 µs
450 µs
600 µs
100 µm

Figure 4

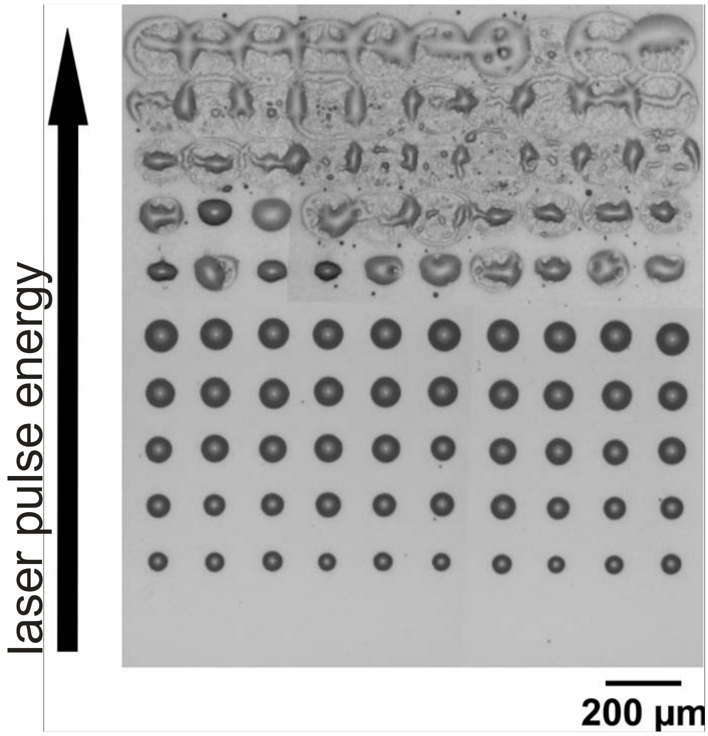

Figure 5