Laser and Particle Beams (2015), *33*, 449–454.

doi:10.1017/S0263034615000476

Micro-patterning of Indium thin film for generation of micron and submicron particles using femtosecond laser-induced forward transfer

KAMLESH ALTI,[1] SUDHANSHU DWIVEDI,[2] SANTHOSH CHIDANGIL,[2] DEEPAK MATHUR,[3] AND ALIKA KHARE[4]

[1]Department of Physics, Sant Gadge Baba Amravati University, Amravati, India
[2]Department of Atomic and Molecular Physics, Manipal University, Manipal, India
[3]Tata Institute of Fundamental Research, Mumbai, India
[4]Department of Physics, Indian Institute of Technology Guwahati, Guwahati, India

(Received 17 December 2014; Accepted 30 April 2015)

Abstract

This paper reports on micro-pattering of Indium thin film (donor substrate) using a higher deposition dose than previously reported. The threshold deposition dose required for micro-patterning was measured. Ejected material from the micro-patterned thin film was deposited onto an accepter substrate kept in close proximity; it clearly shows deposition of micron and submicron particles of Indium. Moreover, a clean line like structure was deposited onto the accepter substrate when the accepter substrate was moved with the same velocity as that of the donor substrate.

Keywords: Indium Thin film; Laser induced forward transfer; Laser micromachining; Micron and submicron particles

1. INTRODUCTION

Laser-induced forward transfer or laser-induced film transfer (LIFT) is a micro/nano printing technique. Usually pulsed laser is focused onto the back side of thin film, which is deposited on the transparent substrate (also called as donor substrate). Interface of the thin film gets heated up due to laser pulse which ultimately melts and vaporizes. The pressure induced by the vapor at the interface ejects the film towards the accepter substrate which is kept sufficiently close to donor substrate.

This method was first demonstrated by Bohandy *et al.* (1986), for depositing copper metal patterns under vacuum using nanosecond excimer laser ($\lambda = 193$ nm) pulses. LIFT was demonstrated in atmospheric condition by the same group using Ag thin films (Bohandy *et al.*, 1988). Later on LIFT was used for a variety of metallic films such as Al (Schultze & Wagner, 1991), W (Tóth *et al.*, 1993; Kántor *et al.*, 1994a), and Cr (Zergioti *et al.*, 1998). All these references cited so far shows that superheating of the donor metal thin film is necessary to realize transfer. Hence LIFT was not seen as a practical option for sensitive and soft materials.

To overcome this, number of modifications in the LIFT techniques have been suggested and implemented which results into multiple variants of the technique. These variants are Matrix-Assisted Pulsed Laser Evaporation-Direct Write (MAPLE-DW) technique (Pique *et al.*, 1999), Dynamic Release Layer-LIFT (Tolbert *et al.*, 1993), Hydrogen Assisted LIFT (Toet *et al.*, 1999), Laser-Induced Thermal Imaging (LITI) technique (Blanchet *et al.*, 2003), Long-Pulsed LIFT (Kántor *et al.*, 1994b; Kántor & Szorenyi, 1995). Variants of the LIFT technique had been tested on diverse varieties of materials, from a gamut of hazardous material (Veiko *et al.*, 2006) to soft biological matter (Colina *et al.*, 2005). Recently, LIFT has been used for fabrication of multilayer metamaterials (Tseng *et al.*, 2012), three-dimensional plasmonic cavities (Chen *et al.*, 2013), miniature sensors and microbattery systems (Piqué *et al.*, 2002), bio-printing (Mézel *et al.*, 2010), and many more.

During their work on the dynamic release method Tolbert *et al.* (1993) showed that laser pulse width has an effect on laser threshold needed for transfer. Laser fluence threshold was found to be order of magnitude smaller than for picoseconds laser pulses compared with nanosecond laser pulses. These findings were verified by other researches using femtosecond laser pulses. Use of femtosecond laser pulses for the LIFT process allows greater precision of energy

Address correspondence and reprint requests to: Kamlesh Alti, Department of Physics, Sant Gadge Baba Amravati University, Amravati 444 602, India. E-mail: kamleshalti@sgbau.ac.in

deposition compared with that of nanosecond pulses (Banks, 2008). Femtosecond-LIFT has successfully been applied recently to transfer bio-materials (Karaiskou *et al*., 2003).

Recently, Thomas *et al*. (2014) demonstrated utilization of only a femtosecond laser oscillator with MHz repetition rate for implementation of LIFT. With low pulse energy (~nJ) but with high pulse frequency (MHz), heat accumulation takes place which ultimately melts the thin film and subsequently ejects it out. This paper explored the effects of laser energy and scanning speed on the efficacy of LIFT and showed that that one can control the LIFT pattern by controlling the relative motion between the acceptor and donor substrates. However, from an applications perspective, it would be more appropriate to combine various experimental parameters such as laser energy, translation speed, laser repetition rate, and focusing conditions into one single parameter to compare results obtained using LIFT instead of, as is currently the vogue in existing literature, merely mentioning a set of single parameters, such as laser energy, speed, repetition rate or focusing conditions. In this paper, the concept of deposition dose is used which slightly differs from energy dose concept used by Thomas *et al*. (2013). This single parameter will be representation of all the experimental conditions used.

Deposition dose can be defined as

$$D_{\text{dose}} = \frac{E_{\text{pulse}} R}{hdv}\ \mu\text{J}\,\mu\text{m}^{-3} \tag{1}$$

where E_{pulse} is the input pulse energy (in μJ), R is the pulse repetition rate (in Hz), v is the speed (in μm s^{-1}) with which donor substrate moves and h is the donor film thickness and d is the laser spot diameter (both in μm). The highest deposition dose reported for LIFT of Indium thin films was ~89.5 μJ μm^{-3} (Thomas *et al*., 2014). This paper reports further experimental work that seeks to probe the following outstanding questions:

- Is surface micro-patterning possible with higher deposition dose values like the sub-surface pattern formation reported by Thomas *et al*. (2013)?
- Will deposition on the accepter substrate also be patterned?
- What will be the effect of movement of accepter substrate along with donor substrate on the re-deposition?

The lowest deposition dose used in the present study is 192.5 μJ μm^{-3}, which is much more than that of reported by Thomas *et al*. (2014).

2. EXPERIMENTAL SET-UP

The experimental set-up used for this work is essentially similar to that described in our earlier report (Thomas *et al*., 2014) with only relatively small modifications. In brief, a high energy Ti: Sapphire femtosecond laser oscillator (800 nm wavelength, 200 nJ output energy, 50 fs pulse duration, 5.2 MHz repetition rate) was used for our LIFT measurements (Fig. 1). A single-shot autocorrelator was used to monitor the laser pulse width. The pulse energy was attenuated with the help of a half wave plate and polarizer assembly. The laser beam was directed towards the sample using suitable optics, as shown in Figure 1, and finally focused

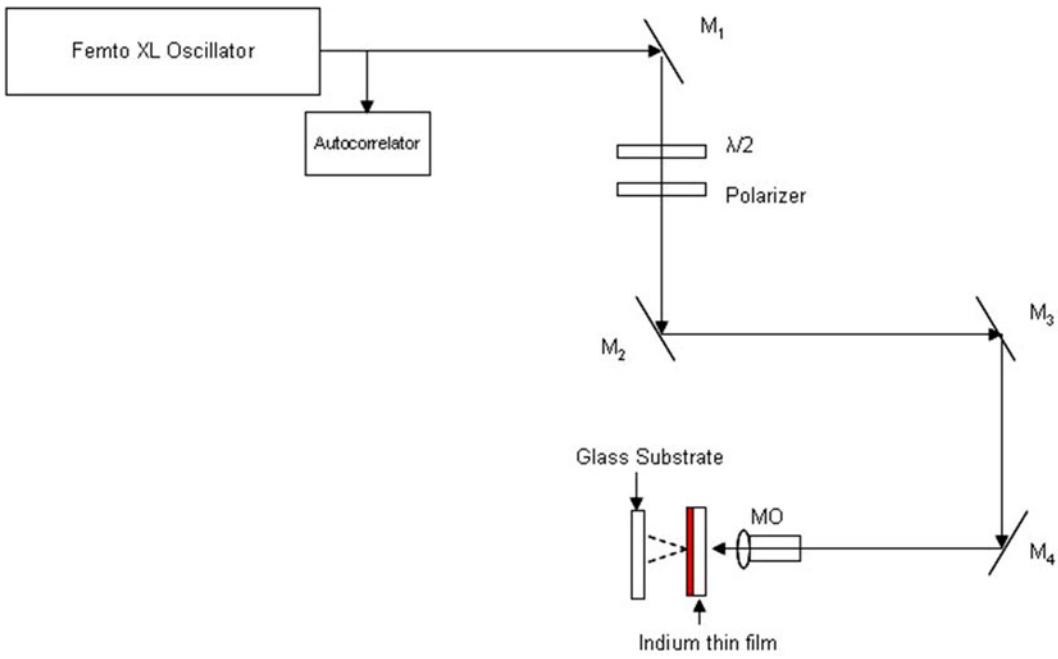

Fig. 1. Schematic depiction of our LIFT experimental set up using a Ti:Sapphire femtosecond laser oscillator.

https://doi.org/10.1017/S0263034615000476 Published online by Cambridge University Press

on the rear side of the donor Indium thin film using a 10X (NA = 0.25) microscopic objective. The focal spot size after the microscopic objective was measured using a beam profiler and it was found to be 2.7 μm. An integrating sphere was used to measure the transmission of the microscope objective; it was found to be 93%.

The Indium thin film (donor) was mounted on a one-dimensional (1D) motorized translation stage. The accepter substrate was kept on another, similar, 1D motorized translation stage. Accepter substrate was kept stationary in one set of experiments while in another, it moved with the same velocity as that of the donor substrate. Measurements were made at different values of laser energy. The distance between the accepter substrate and the donor thin film was kept constant to within 400 μm.

The Indium thin film used in this work was deposited on cleaned microscope glass slides (size 2.5×7.5 cm) via a thermal evaporation coating unit kept at a base pressure of 10^{-6} Torr. Indium metal used for the deposition was of 99.995% purity (purchased from Nuclear Fuel Complex, Hyderabad). Thickness of the thin films was found to be 2 μm. Machined donor substrates and LIFT patterns on acceptor substrates were characterized using optical microscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray diffraction (EDAX).

3. RESULTS AND DISCUSSIONS

Often, femtosecond micromaching at MHz repetition rate is compared with KHz repetition rate. In KHz machining individual pulses are responsible for inducing change in the refractive index of the material, whereas in MHz regime, cumulative effect of many pulses is responsible for index change of the material. Due to dominant cumulative effects, heating of the material has been observed which leads to melting and subsequent re-solidification (Eaton *et al*., 2005).

In this work, micron sized line structure was written on the donor Indium thin film by focusing the femtosecond laser pulses via a 10X microscopic objective from the rear side of the Indium thin film, as shown in Figure 1. Line structures were written at different values of incident laser energy, with values which varied over the range 60–166 nJ. During the

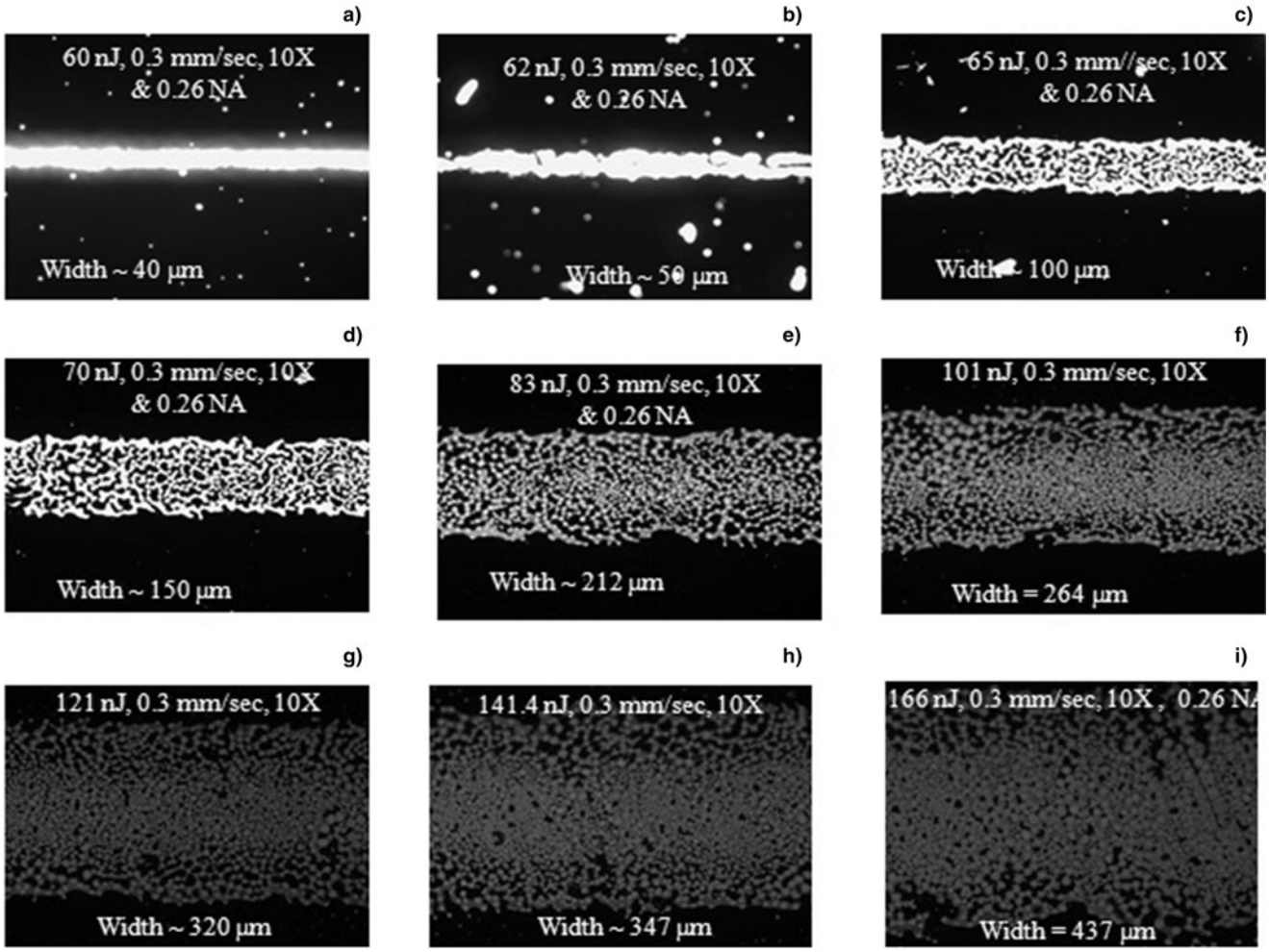

Fig. 2. Micrograph showing modified region of Indium thin film when femtosecond laser pulses of energy; (a). 60 nJ, (b). 62 nJ, (c) 65 nJ, (d) 70 nJ, (e) 83 nJ, (f) 101 nJ, (g) 121 nJ, (h) 141 nJ, and (i) 166 nJ were used for machining.

https://doi.org/10.1017/S0263034615000476 Published online by Cambridge University Press

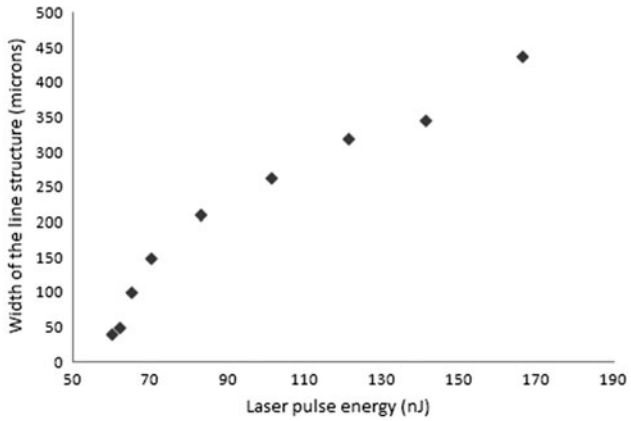

Fig. 3. Graph showing increase in the width of line structure written on donor substrate with increase in the laser pulse energy.

course of each experiment, the donor thin film was moved at a constant speed of 0.3 mm s^{-1}, a value that is significantly lower than previously used by us (Thomas *et al*., 2014). Figure 2 shows typical optical micrographs of the machined donor thin films with 10X magnification for different laser energies. The dark region in each micrograph indicates presence of Indium while the bright region corresponds to absence of it. Laser pulse energy was increased from 60 to 166 nJ as one go from Figures 2a to 2i. With just 5 nJ increase in the laser pulse energy, the width of the machined region was found to increase from 40 to 100 μm, as seen in images shown in Figures 2a and 2c. More interestingly, grain/mesh like structure is seen in Figure 2c whereas Figure 2a shows a clean, machined region with no visible leftovers at 10X magnification. Thereafter, all the subsequent images show similar grain/mesh like structure. Width of the machined region was found to increase with increase in laser pulse energy as shown in Figure 3. In a report by Thomas *et al*. (2013), sub-surface patterning of glass has been reported at higher energies. In this article, varieties of sub-surface patterns were reported in different transparent materials. As reported, such patterns were obtained only if energy dose is above a certain fixed value. Below which, the change in the refractive index was found to be smooth and continuous and as it goes above certain threshold value, it becomes discontinuous pearl/rod like structures. However, these results were reported for bulk transparent material. Figure 2 reports similar transition but for a thin film.

From Figure 2, it is quite clear that the micro-pattering of the donor substrate only becomes possible when the deposition dose is equal to or above 210 μJ μm^{-3} (corresponds to Fig. 2c–i). The highest deposition dose used in this experiment (Fig. 2i) corresponds to 532 μJ μm^{-3}.

Next the accepter substrate, which was kept 400 μm away from the donor thin film, was analyzed. The accepter substrate was kept stationary during this experiment. SEM images of the accepter substrate (corresponding to the donor substrate shown in Fig. 2i) were acquired and are shown in Figure 4. These images confirm deposition of Indium particles on the accepter substrate. Spattered deposition of Indium particles on the accepter substrate correlates to micro-patterned donor substrate (Fig. 2i). Micron and few submicron size particles are clearly visible in the SEM images. EDAX measurement confirms presence of Indium on the accepter substrate.

In a different experimental set, accepter substrate was moved with the same velocity as that of the donor substrate, namely 0.3 mm s^{-1}, during transfer. Forty linear structures were written on the donor substrate using a deposition dose of 192.5 μJ μm^{-3}, which is below the micro-pattering threshold. At this deposition dose, machined donor substrate looks similar to as shown in Fig. 2a. Each time, to write a new linear structure, the donor substrate was laterally displaced so as to get the next unexposed thin film region for transfer: The accepter substrate was not moved laterally during the entire experiment. This implies that the ejected material from all the 40 line structures written on the donor substrate might have got deposited linearly on the accepter substrate at one location. SEM images were recorded for the accepter substrate and a typical image is shown in Figure 5. It shows linear deposition of material, in conformity with our expectation. The width of this structure is nearly 1 μm. It should be noted again that at 192.5 μJ μm^{-3} deposition

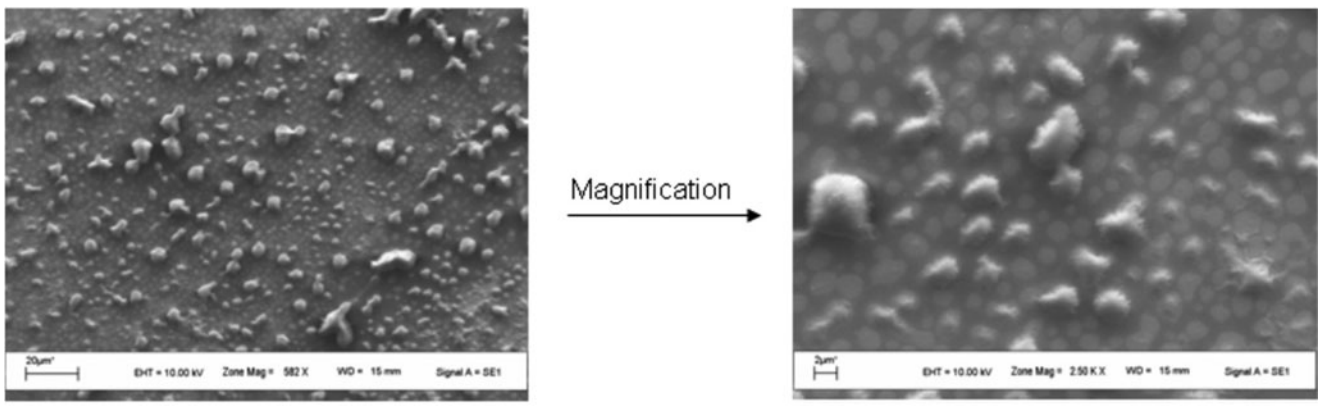

Fig. 4. SEM images of accepter substrate showing deposition of micro and some submicron particles at two different magnifications.

https://doi.org/10.1017/S0263034615000476 Published online by Cambridge University Press

Fig. 5. SEM image of accepter substrate showing linear deposition.

dose value, there was clean ejection of material from the donor substrate, as seen in Figure 2a. It seems that the ejected material from all the written 40 lines coalesced and compressed to a single line structure with a width of just 1 μm. A similar experiment was done before by Tan *et al*. (2003), in which they have used maximum deposition dose of ~44.5 μJ μm^{-3} to deposit micro lines of gold on the accepter substrate. Deposition dose used in this paper to produce micro lines of Indium is much more than that used by Tan *et al*. (2003). However micro line structure in our case is much cleaner, compress and coalesce compared with work presented in Tan *et al*. (2003).

4. CONCLUSION

The experimental work reported here suggests that as in the case of sub-surface pattern formation using a femtosecond laser, surface machining also requires a threshold deposition dose. Micro-patterning is possible at or above this threshold deposition dose. In the case of Indium deposition in our experiments, the threshold deposition dose was found to be 210 μJ μm^{-3}. This value may vary for different thickness of thin film or for different thin film material. Spattered micron and submicron particles of Indium were observed on the acceptor substrate, which correlated with the micro-patterned donor substrate. Interesting, clean line-like deposition having width of ~1 μm was seen on the acceptor substrate when it was moved at the same velocity as that of the donor substrate during the experiment. Therefore this technique has potential application in fabrication of optoelectronic and photonic devices.

ACKNOWLEDGEMENT

This work constituted part of the activities of I-CUP, the Indian Cluster for Ultrafast Photonics, which was supported by the Office of the Principal Scientific Adviser to the Government of India.

REFERENCES

Banks, D.P. (2008). Femtosecond laser induced forward transfer techniques for the deposition of nanoscale, intact, and solid phase material. Ph.D. thesis. Southampton: University of Southampton.

Blanchet, G., Loo, Y.-L., Rogers, J., Gao, F. & Fincher, C. (2003). Large areas, high resolution, dry printing of conducting polymers for organic electronics. *Appl. Phys. Lett*., **82**, 463–465.

Bohandy, J., Kim, B.F. & Adrian, F.J. (1986). Metal deposition from a supported metal film using an excimer laser. *J. Appl. Phys*., **60**, 1538–1539.

Bohandy, J., Kim, B.F., Adrian, F.J. & Jette, A. (1988). Metal deposition at 532 nm using a laser transfer technique. *J. Appl. Phys*., **63**, 1158–1162.

Chen, W., Tseng, M., Liao, C., Wu, P., Sun, S., Huang, Y., Chang, C., Lu, C., Zhou, L., Huang, D., Liu, A. & Tsai, D. (2013). Fabrication of three-dimensional plasmonic cavity by femtosecond laser-induced forward transfer. *Opt. Express*, **21**, 618–625.

Colina, M., Serra, P., Fernández-Pradas, J.M., Sevilla, L. & Morenza, J.L. (2005). DNA deposition through laser induced forward transfer. *Biosensors Bioelectron*., **20**, 1638–1642.

Eaton, S., Zhang, H., Herman, P., Yoshino, F., Shah, L., Bovatsek, J. & Arai, A. (2005). Heat accumulation effects in femtosecond laser-written waveguides with variable repetition rate. *Opt. Express*, **13**, 4708–4716.

Kántor, Z. & Szorenyi, T. (1995). Dynamics of long-pulse laser transfer of micrometer-sized metal patterns as followed by time-resolved measurements of reflectivity and transmittance. *J. Appl. Phys*., **78**, 2775–2781.

Kántor, Z., Toth, Z. & Szorenyi, T. (1994a). Metal pattern deposition by laser-induced forward transfer. *Appl. Surf. Sci*., **86**, 196–201.

Kántor, Z., Tóth, Z., Szorenyi, T. & Tóth, A.L. (1994b). Deposition of micrometer-sized tungsten patterns by laser transfer technique. *Appl. Phys. Lett*., **64**, 3506–3508.

Karaiskou, A., Zergioti, I., Fotakis, C., Kapsetaki, M. & Kafetzopoulos, D. (2003). Microfabrication of biomaterials by the sub-ps laser-induced forward transfer process. *Appl. Surf. Sci*., **208–209**, 245–249.

Mézel, C., Souquet, A., Hallo, L. & Guillemot, F. (2010). Bioprinting by laser-induced forward transfer for tissue engineering applications: Jet formation modeling. *Biofabrication*, **2**, 014103(1)–014103(7).

Piqué, A., Arnold, C.B., Wartena, R.C., Weir, D.W., Pratap, B., Swider-Lyons, K.E., Kant, R.A. & Chrisey, D.B. (2002). Laser-induced forward transfer direct-write of miniature sensor and microbattery systems. *Proc. Third Int. Symp. Laser Precision Microfabrication Int. Soc. Opt. Eng*. (*SPIE*), **4830**, 182–188.

Pique, A., Chrisey, D., Auyeung, R., Fitz-Gerald, J., Wu, H., McGill, R., Lakeou, S., Wu, P., Nguyen, V. & Duignan, M. (1999). A novel laser transfer process for direct writing of electronic and sensor materials. *Appl. Phys. A [Suppl.]*, **69**, S279–S284.

Schultze, V. & Wagner, M. (1991). Laser-induced forward transfer of aluminum. *Appl. Surf. Sci*., **52**, 303–309.

Tan, B., Venkatakrishnan, K. & Tok, K.G. (2003). Selective surface texturing using femtosecond pulsed laser induced forward transfer. *Appl. Surf. Sci*., **207**, 365–371.

Toet, D., Thompson, M., Smith, P. & Sigmon, T. (1999). Laser-assisted transfer of silicon by explosive hydrogen release. *Appl. Phys. Lett*., **74**, 2170–2172.

https://doi.org/10.1017/S0263034615000476 Published online by Cambridge University Press

Tolbert, W., Lee, I., Doxtader, M., Ellis, E. & Dlott, D. (1993). High-speed color imaging by laser ablation transfer with a dynamic release layer: Fundamental mechanisms. *J. Imag. Sci. Tech*., **37**, 411–421.

Tóth, Z., Szorenyi, T. & Tóth, A.L. (1993). Ar^+ laser-induced forward transfer (LIFT): A novel method for micrometer-size surface patterning. *Appl. Surf. Sci*., **69**, 317–320.

Tseng, M.L., Wu, P.C., Sun, S., Chang, C.M., Chen, W.T., Chu, C.H., Chen, P.L., Zhou, L., Huang, D.W., Yen, T.J. & Tsai, D.P. (2012). Fabrication of multilayer metamaterials by femtosecond laser-induced forward-transfer technique. *Laser Photon. Rev*., **6**, 702–707.

Thomas, J., Bernard, R., Alti, K., Dharmadhikari, A.K., Dharmadhikari, J.A., Bhatnagar, A., Santhosh, C. & Mathur, D. (2013). Pattern formation in transparent media using ultrashort laser pulses. *Opt. Commun*., **304**, 29–38.

Thomas, J., Bernard, R., Thomas, J.T., Alti, K., Santhosh, C., Kumari, S., Khare, A. & Mathur, D. (2014). Femtosecond Laser Induced Forward Transfer of Indium thin films. *Laser Part. Beams*, **32**, 55–61.

Veiko, V.P., Shankhno, E.A., Smirnov, V.N., Miaskovski, A.M. & Nikishin, G.D. (2006). Laser–induced film deposition by LIFT: Physical mechanisms and applications. *Laser Part Beams*, **24**, 203–209.

Zergioti, I., Mailis, S., Vainos, N.A., Papakonstantinou, P., Kalpouzos, C., Grigoropoulos, C.P., & Fotakis, C. (1998). Microdeposition of metal and oxide structures using ultrashort laser pulses. *Appl. Phys. A*, **66**, 579–582.