Triazene photopolymer dynamic release layer-assisted femtosecond laser-induced forward transfer with an active carrier substrate

A Letters Journal Exploring the Frontiers of Physics

August 2008

EPL, **83** (2008) 38003
doi: 10.1209/0295-5075/83/38003

www.epljournal.org

Triazene photopolymer dynamic release layer-assisted femtosecond laser-induced forward transfer with an active carrier substrate

D. P. Banks[1(a)], K. Kaur[1], R. Gazia[1], R. Fardel[2,3], M. Nagel[2], T. Lippert[3] and R. W. Eason[1]

[1] *Optoelectronics Research Centre, University of Southampton - Southampton SO17 1BJ, UK, EU*
[2] *General Energy Research Department, Paul Scherrer Institut - 5232 Villigen PSI, Switzerland*
[3] *EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Functional Polymers Überlandstrasse 129, 8600 Dübendorf, Switzerland*

received 18 March 2008; accepted in final form 13 June 2008
published online 23 July 2008

PACS 81.15.Fg – Laser deposition
PACS 64.70.km – Polymers
PACS 42.65.Ky – Frequency conversion; harmonic generation, including higher-order harmonic generation

Abstract – Discs of solid material have been forward transferred from thin films on transparent carrier substrates using femtosecond Ti:sapphire laser-induced forward transfer (fs-LIFT) with a triazene polymer dynamic release layer (DRL). The fluence threshold for fs-LIFT was found to be only $\approx 20\%$ of the DRL ablation threshold at the laser wavelength. This decrease is attributed to ultrafast shock-wave generation in the constrained polymer layer under femtosecond irradiation being the driving force for fs-LIFT with the polymer DRL. The result is very different from the nanosecond regime, where the LIFT threshold is observed to be slightly above the polymer ablation threshold. White-light continuum generation in a carrier substrate is observed and its influence on the fs-LIFT process is discussed.

Introduction. – The deposition of patterned thin films of various materials is important for both fundamental research and technical (*i.e.* micro-electro-mechanical) applications. Most techniques applied for this purpose lack lateral resolution on micron and smaller scales, so separate deposition and patterning stages are necessary. Direct-write (DW) methods are attractive for microdeposition applications as deposition and patterning can be achieved simultaneously.

A very promising technique offering sub-micron lateral resolution deposition of a wide variety of materials is laser-induced forward transfer (LIFT) (fig. 1(a)) [1]. In LIFT, a thin film of the material to be deposited (the donor) is coated onto a transparent carrier substrate. The coated carrier is placed in close contact with a receiving substrate and one or more focused or demagnified laser pulses are used to transfer a well-defined section of the film. The laser induces ablation at the carrier-film interface to propel material to the receiver.

Whilst LIFT is readily applied for metal films [1,2] and materials that are heat-resistant, sensitive materials such as biomaterials, organic dyes, and semiconducting polymers can be damaged by the laser irradiation. The high pressures and temperatures that are experienced by the donor during transfer can result in photo- or thermo-chemical reactions, phase-changes and evaporation. As such, it is now relatively common practice in LIFT experiments to include a sacrificial propellant material, either in the form of a supporting matrix (Matrix-Assisted Pulsed Laser Evaporation-Direct Write

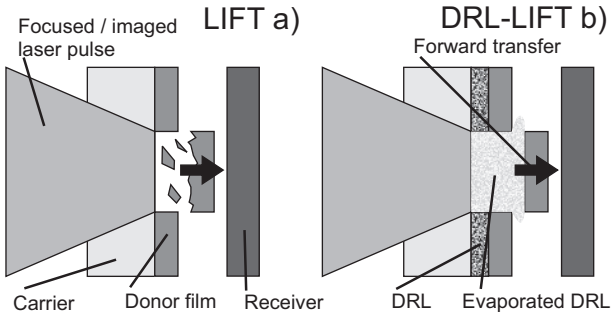

Fig. 1: Schematics of LIFT (a) and DRL-assisted LIFT (b).

(a) E-mail: dpb@orc.soton.ac.uk

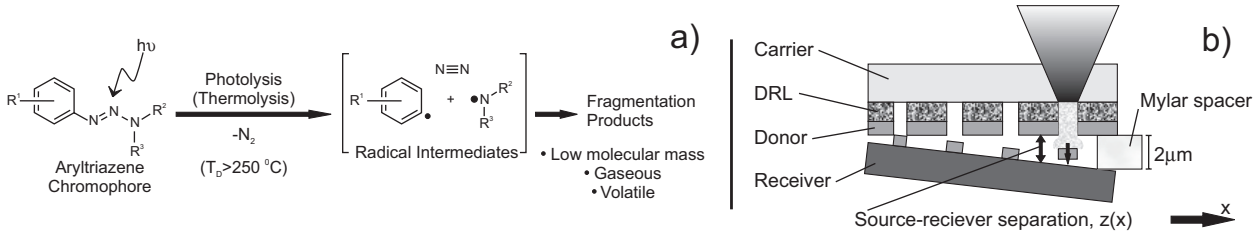

Fig. 2: Photolytic cleavage pathway of a triazene chromophore (the chromophore can also experience thermal decomposition above about 250 °C) (a) [7]. Experimental layout used to study femtosecond LIFT with TP DRL (b).

(MAPLE-DW)) [3,4], or as a separate layer between carrier and donor (a dynamic release layer (DRL)) [5], to protect the active material during transfer. DRL-LIFT is shown schematically in fig. 1(b).

Dynamic release layers. – To be suitable for use as a DRL, a material must have a low ablation threshold, high-absorption coefficient, and avoid excessive thermalization of the absorbed photons to facilitate transfer with low thermal impact on the donor. The DRL should also dissociate upon irradiation to avoid contamination of the transferred donor with residual DRL material. A particularly well-suited material for DRL applications is the triazene polymer (TP), which exhibits clean and well-defined photofragmentation into small, volatile, gaseous, molecular fragments. The fragmentation process releases N_2, providing the thrust required for LIFT [6,7]. This thrust, which originates from the pressure increase, allows a precise "cutting" of well-defined regions from the film. The photolytic cleavage pathway of a TP chromophore is shown in fig. 2(a) [7]. The TP chromophore can also experience the same decomposition pathway if the temperature is raised above $\approx 250\,^{\circ}\mathrm{C}$.

The TP has a very low ablation threshold of $25\,\mathrm{mJ/cm^2}$ at 308 nm irradiation (with ns pulses) meaning that transfer can be achieved with low thermal impact on sensitive donors using UV wavelengths [8]. The IR damage threshold of the TP has been measured to be $\approx 500\,\mathrm{mJ/cm^2}$ at 800 nm with 130 fs pulses, with multi-photon absorption believed to be the dominant absorption mechanism [9]. The quality of the structures obtained with fs laser ablation is also quite high, with strong indication that the fs-pulse induced decomposition also produces mainly gaseous ablation products (similar to 308 nm, ns irradiation) [8].

The TP has been used as a DRL in a number of LIFT studies for forward transfer of other polymers [10], cells [11], quantum dots [12], and organic LEDs [13]. Other materials have also been used as DRLs, including metals [14,15], hydrogenated silicon [16], and other polymers [5,17]. An important point to note is that in all these studies, which used nanosecond pulsed lasers, the fluence threshold required for LIFT was slightly greater than the normal ablation threshold of the DRL material. This result should not be surprising as, to achieve forward transfer, sufficient DRL material must be ablated to provide LIFT thrust.

In this work, we present results using the TP as a DRL for the forward transfer of "hard" donor films. An 800 nm femtosecond pulsed laser is used, representing the first ultrashort-pulsed TP DRL results. The different transfer mechanisms in the nanosecond and femtosecond regimes will be discussed. Before the fs-LIFT results are presented, we shall discuss the occurrence of nonlinear optical phenomena in the carrier. Such phenomena are unavoidable in a typical fs-LIFT setup, but their potential consequences have not yet been considered in the literature.

Experimental. – For all LIFT experiments, single pulses from a Ti:sapphire laser (800 nm, ≈ 130 fs) were used. Spatially-Gaussian laser pulses of ≈ 4 mm diameter (FWHM) were centrally incident on a 450 μm circular aperture, resulting in a circular beam; the intensity difference between the centre and the edge of the beam was $\approx 5\%$. A highly demagnified image of the aperture was relayed to the target using a reverse projection microscope resulting in an $\approx 12\,\mu$m diameter circular spot at the carrier-film interface, as measured by the laser damaged area. The image plane of the microscope was adjusted to coincide with the best image of the aperture and the depth of focus of the laser was measured to be $\approx 200\,\mu$m.

The TP was synthesized as described by Nagel *et al.* [6] and was then prepared by spin coating from a solution in chlorobenzene and cyclohexanone (1 : 1, w/w). The thickness of the TP was controlled by adjusting the viscosity of the solution and spin speed to yield a DRL with a thickness of ≈ 100 nm. The carrier substrates were a fused quartz disc (diameter 50 mm, thickness 3 mm) and the receiver was a Si wafer ≈ 10 mm square. All experiments were performed under vacuum at ≈ 0.1 mbar. The separation between the donor film and the receiver, z, was controlled by the insertion of a single 2 μm thick Mylar spacer. This resulted in a variation of the separation with position across the LIFT setup, $z(x)$, as shown in fig. 2(b). Donor-receiver separation was measured interferometrically using the microscope's white-light source.

On top of each DRL, a donor film of ≈ 150 nm of a transparent amorphous GdGaO material was grown by pulsed laser deposition (PLD). The PLD target was single crystal gadolinium gallium garnet ($Gd_3Ga_5O_{12}$). The films were deposited at room temperature and in an oxygen

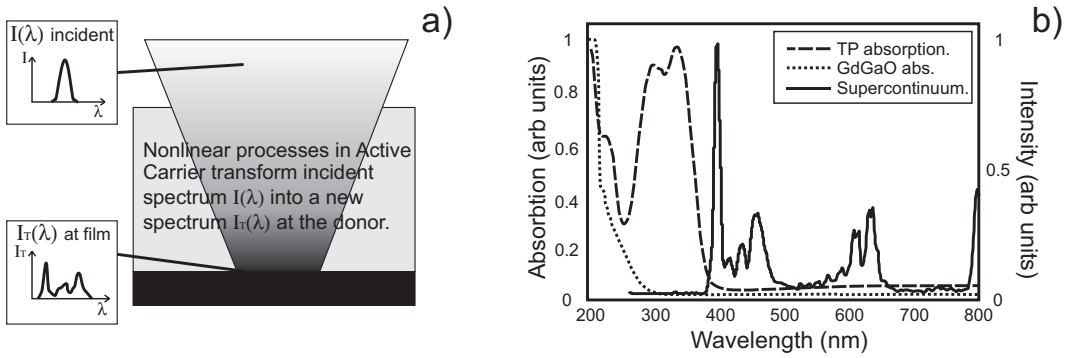

Fig. 3: Schematic of the active carrier technique (a). Typical measured supercontinuum spectrum (solid line), and TP (dashed line) and GdGaO (dotted line) film absorption curves (b).

atmosphere at a pressure of 4×10^{-2} mbar. The GdGaO was chosen as a sample material to study the fs-LIFT of "hard" donor films using the TP-DRL. It is interesting because it can be grown under conditions that do not damage the polymer and LIFTed in the amorphous state before post-transfer annealing to crystallise it (results not presented here). As such it may provide a template for the micro-deposition of single-crystal material by fs-LIFT.

Active carriers. – The measured ablation threshold of the TP at 800 nm corresponds to an intensity of $\approx 10^{12}\,\mathrm{W/cm^2}$ [9]. Reported intensity thresholds for femtosecond LIFT are also typically $\geqslant 10^{11}\,\mathrm{W/cm^2}$ (see *e.g.* [2,18–21]). It is well-known that, when ultrashort laser pulses are focused inside transparent media, supercontinuum generation can occur, resulting in a significant broadening of the laser spectrum [22]. The intensity threshold for the onset of supercontinuum generation with 800 nm in silica has been measured to be $\approx 10^{11-12}\,\mathrm{W/cm^2}$ and, a spectrum from $\approx$ 400–950 nm is generated [23]. Hence, in a fs-LIFT arrangement it is unavoidable that, at some point within the carrier, the laser intensity will be great enough to generate a supercontinuum. Such a setup, where the normally passive carrier substrate plays an active role by modifying the laser spectrum, may be termed active carrier LIFT (AC-LIFT). The principle of AC-LIFT is indicated in fig. 3(a).

To measure the spectrum and intensity of the supercontinuum generated in the current experiment, the laser was imaged onto the rear surface of an uncoated carrier in exactly the same geometry as used for all fs-LIFT experiments. Two IR cut-off filters (cut-off wavelength $\approx$ 670 nm; effective transmission (800 nm) $\leqslant 1\%$, ($\leqslant$ 670 nm) $\geqslant 90\%$) were inserted after the uncoated carrier to remove residual 800 nm light. The threshold for supercontinuum generation was measured to be $\approx 110\,\mathrm{mJ/cm^2}$ ($\cong 7 \times 10^{11}\,\mathrm{W/cm^2}$). The conversion efficiency (including all wavelengths $\leqslant$ 670 nm) was $\approx$ 1–1.5%. The solid trace in fig. 3(b) shows a typical spectrum; the supercontinuum displayed a strong peak around 400 nm with an intensity $\leqslant 1\%$ of the incident laser. The new wavelengths generated in the AC represent another possible source of laser-induced damage to the donor material that must be considered when choosing the combination of donor and DRL materials, and laser wavelength.

The absorption spectrum of the GdGaO donor film is also shown in fig. 3(b), dotted line. As can be seen, the material was essentially transparent to wavelengths longer than 300 nm; hence the donor could not be damaged either directly by the laser or by the AC-generated supercontinuum. The absorption spectrum of the TP polymer is represented by the dashed line in fig. 3(b) [9]. The TP did not significantly absorb the AC-generated supercontinuum. The absorption coefficients at 400 nm and 800 nm were approximately equal; hence, given the $\approx 1\%$ conversion efficieny from 800 $\rightarrow$ 400 nm, it can be concluded that the AC did not affect linear absorption of the laser in the TP-DRL. The measured ablation threshold for a 100 nm thick TP film with no overlying donor irradiated through a carrier substrate was found to be $\approx 500\,\mathrm{mJ/cm^2}$. This value was in good agreement with the normal ablation threshold at 800 nm and significantly above the threshold for onset of supercontinuum generation, deomnstrating that the presence of the continuum did not significantly affect the TP ablation.

GdGaO results. – The threshold for forward transfer of the GdGaO donor was measured to be $\approx 90\,\mathrm{mJ/cm^2}$ with the TP-DRL and $\approx 110\,\mathrm{mJ/cm^2}$ without it. Figure 4(a) shows an SEM image of transferred GdGaO material using $\approx 120\,\mathrm{mJ/cm^2}$ without the DRL, and fig. 4(b,c) show SEM micrographs of GdGaO discs deposited with the DRL; fluence $\approx$ 90–100 $\mathrm{mJ/cm^2}$. The donor-receiver separation was $\approx$ 100–200 nm. The benefits of using the TP-DRL for the LIFTing of solid material from hard donor films are apparent. Surface profiling of typical discs transferred using the DRL, similar to those in fig. 4(b,c), is shown in fig. 4(d). The deposits were reproducibly $\approx$ 130 nm thick, closely matching the original thickness of the GdGaO donor and indicating that little or no DRL remained on the deposit post-transfer. Another reproducible feature of the deposits was a slightly raised region around the edge, which is believed to be a result of

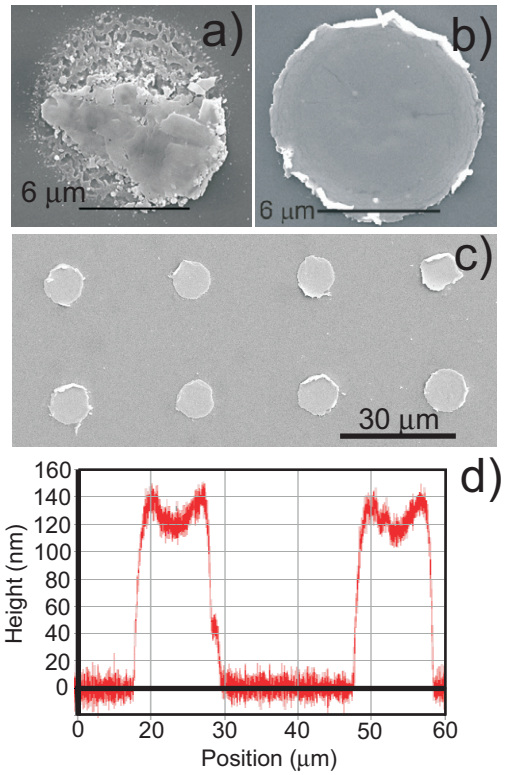

Fig. 4: SEM micrographs of GdGaO deposition without a TP-DRL ($\approx 120\,\mathrm{mJ/cm^2}$) (a), and with the DRL (≈ 90–$100\,\mathrm{mJ/cm^2}$) (b,c); donor-receiver separation of ≈100–200 nm. Surface profiling of deposits like those shown in (c) (d).

how the deposits were transferred, which will be discussed later.

The most important thing to note with regards to the GdGaO depositions is the significant difference in laser fluence threshold for forward transfer and direct ablation of the TP ($\approx 500\,\mathrm{mJ/cm^2}$ [9]); the LIFT threshold was only about 20% of the direct ablation threshold. This was very different from the case of nanosecond polymer DRL-assisted LIFT where the LIFT threshold has been consistently found to be slightly above the polymer ablation threshold. Hence a totally new process is observed when using femtosecond pulses for TP DRL-LIFT. The reason for the dramatically lower LIFT threshold with femtosecond pulses is hypothesised as follows, and shown schematically in fig. 5.

1. fig. 5(1): The incident laser energy was absorbed in the TP DRL through multi-photon absorption of the 800 nm laser; for reasons discussed earlier, the AC-generated supercontinuum is not thought to play a significant role. Furthermore, interface effects and multiple reflections from the TP-donor and donor-vacuum interfaces, and the Si receiver may have slightly increased absorption in the DRL.
2. fig. 5(2): As the absorption depth of the laser significantly exceeded the film thickness, absorption throughout the irradiated region was approximately homogeneous.
3. fig. 5(3): The absorption of ultrashort duration pulses in polymers initiates a rapid pressure jump in the target due to the pulse energy being deposited faster than the target can fully relax (see *e.g.*, [24]). This is in sharp contrast to exposure to longer duration pulses, where the relatively slow rate of energy deposition predominantly results in a temperature increase. However, even with ultrashort pulses, with free surface ablation this pressure increase can be somewhat relaxed by expansion of the target. In a DRL-LIFT arrangement, particularly with a hard donor film, significant expansion of the polymer is restricted by the overlying layer. Hence in this case, the pressure of the TP DRL was raised sharply by absorbing the femtosecond pulse. The increase could not be easily relaxed by polymer expansion, so a sharp temperature increase in the TP occurred.
4. fig. 5(4): This temperature increase resulted in the DRL temperature rising above $\approx 250\,^\circ\mathrm{C}$ and thermolytic decomposition of the DRL occurred.

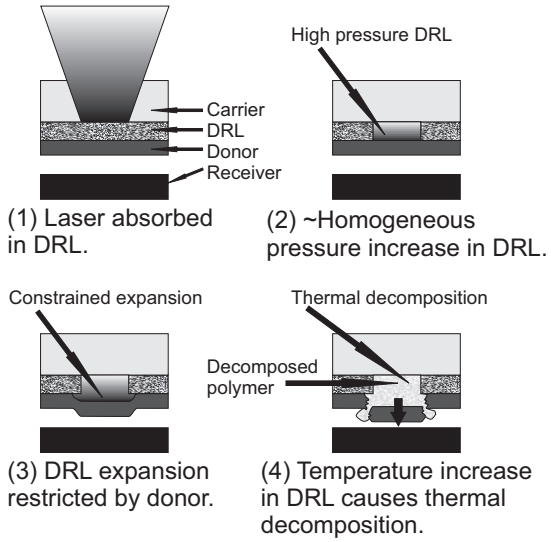

Fig. 5: Hypothesised process leading to low forward transfer threshold fluence when using ultrashort pulses.

Hence we envisage a situation where absorption of the femtosecond pulse initiated a rapid pressure jump in the TP which could not be easily relaxed due to the overlying donor layer. The polymer temperature then increased and thermal decomposition of the TP chromophores occurred well below the DRL ablation threshold.

To further support the hypothesis of thermal decomposition resulting from constrained pressure increase being the driving force for sub-ablation threshold forward transfer with femtosecond pulses, the influence of donor-receiver separation on any resultant GdGaO depositions was studied. The results are shown in fig. 6. Figure 6(a) shows

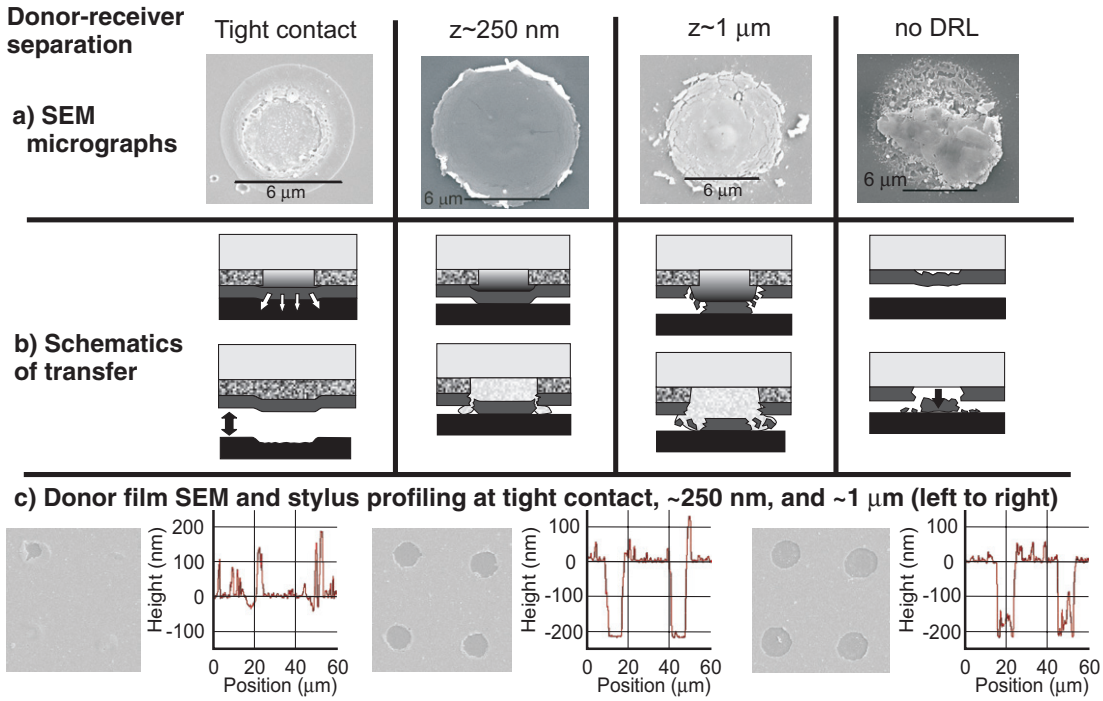

Fig. 6: SEM micrographs (a) and schematics of the forward transfer process (b) with varying donor-receiver separation. (c) SEM and stylus profiling of donor film after LIFT in tight contact (left), at optimal separation, and with greater than optimal separation (right).

SEM micrographs of deposits obtained with tight-contact between donor and receiver (left column), and separations of $\approx 250\,\text{nm}$ & $\approx 1\,\mu\text{m}$. Figure 6(b) shows diagrams of the envisaged transfer process in the different donor-receiver separation regimes. The case of no DRL is also shown for comparison (right column).

When donor and receiver were in tight contact, no discs of donor material were obtained. The TP decomposed due to the large pressure increase, however the tight contact with the receiver prevented expansion of the decomposed polymer, which was necessary to shear the donor. Instead the high pressure build up in the irradiated region just caused some damage to the underlying receiver. EDX analysis and surface-profiling confirmed that there was little or no GdGaO deposited onto the receiver. With a small donor-receiver separation ($\leqslant 500\,\text{nm}$), there was sufficient space for a small amount of expansion of the decomposed polymer which allowed for relatively clean shearing and transfer of a clean disc of donor. The slight deformation of the donor film prior to shearing also explains the slightly raised edges seen around clean disc deposits (see fig. 4(d)). As the separation was increased, the brittle donor experienced increased deformation due to the pressure of the trapped decomposed DRL. With separations of $\approx 1\,\mu\text{m}$, the amount of deformation became sufficiently great that the donor disc shattered during transfer, resulting in a more particulate deposit.

In this case, the optimal donor-receiver separation was found to be around 250 nm. However, it should be noted that the optimal separation is expected to vary with a number of properties including DRL and donor materials and layer thicknesses; for example, less brittle donors should be able to withstand increased deformation without shattering. The size of the laser spot will also affect the deformation of the donor and should have an influence on the dependence of the transfer process on separation.

Figure 6(c) shows SEM and stylus profiling observations of the donor film after LIFT in tight contact (left), at optimal separation, and at greater than optimal separation (right). It can be seen that, in tight contact, most of the GdGaO film remained on the carrier, although a significant roughening of the donor surface was apparent in the irradiated areas. When the separation was increased to optimal, the donor material was completely removed from the carrier apart from small sections around the edge of the irradiated region, which, although fragmented, remained partially attached to the donor film. At greater than optimal separation, complete removal of material in the irradiated region was also seen, but the fragments around the edge were no longer visible attached to the donor and appeared instead as debris on the carrier and donor. The fragmentation of donor material around the edge of the transferred region supports the hypothesis of deformation of the donor, primarily at the edge, occurring as a result of increased pressure of the underlying polymer. We conclude therefore that the Si receiver also played a critical role in determining the final quality of deposited material. The receiver had to be close enough to constrain deformation of the brittle donor and restrict shattering around the edge due to excessive bending. However, a

small separation between donor and receiver was necessary to allow the donor to shear.

A final point to note is that, at optimal donor-receiver separation, stylus profiling results indicated that the TP was completely removed during LIFT (see fig. 4(d) and fig. 6(c)), which is important to avoid contamination of transferred material.

Conclusions. – Discs of GdGaO of $\approx 10\,\mu$m diameter have been deposited by TP DRL-assisted femtosecond LIFT. The use of the TP-DRL allowed for the deposition of pellets of GdGaO in solid phase with no shattering when the donor and receiver were at the optimal separation. In contrast, when no DRL was used GdGaO material was transferred in many fragments due to explosive ablation of the donor material being the driving force for LIFT.

The threshold transfer fluence with the TP-DRL was found to be $\approx 90\,\mathrm{mJ/cm^2}$, only $\approx 20\%$ of the polymer ablation threshold at the laser wavelength. This was in stark contrast to nanosecond DRL-LIFT using this polymer where the transfer threshold is reproducibly found to be slightly greater than the ablation threshold. A model to explain the reduced fluence threshold of TP-DRL fs-LIFT has been proposed based on a rapid increase of the polymer DRL pressure following irradiation that cannot be easily relaxed due to the presence of the overlying donor film and receiver. The model has been supported by the observed morphology of the transferred material and donor film after LIFT. The optimal donor-receiver separation was found to be around 250 nm, although this optimal value is predicted to vary with donor and DRL materials and feature size. The TP has been observed to be removed completely during LIFT.

Supercontinuum generation in the carrier substrate has been observed at the typical transfer fluences. Although the influence of the continuum has been shown to be negligible within this study, the presence of a supercontinuum in a fs-LIFT setup cannot be neglected as the generated wavelengths may be absorbed by the DRL or donor.

* * *

The authors are grateful to the Engineering and Physical Sciences Research Council, UK, for research funding under Grant No. EP/C515668/1. The financial support of the Swiss National Science Foundation is acknowledged.

REFERENCES

[1] Bohandy J., Kim B. F. and Adrian F. J., *J. Appl. Phys.*, **60** (1986) 5138.

[2] Banks D. P., Grivas C., Mills J. D., Zergioti I. and Eason R. W., *Appl. Phys. Lett.*, **89** (2006) 193107.

[3] Piqué A., Chrisey D. B., Auyeung R. C. Y., Fitz-Gerald J., Wu H. D., McGill R. A., Lakeou S., Wu P. K., Nguyen V. and Duignan M., *Appl. Phys. A (Suppl.)*, **69** (1999) S279.

[4] Arnold C. B., Kim H. and Piqué A. , *Appl. Phys. A*, **79** (2004) 417.

[5] Tolbert W. A., Lee I.-Y. S., Doxtader M. M., Ellis E. W. and Dlott D. D., *J. Imaging Sci. Technol.*, **37** (1993) 411.

[6] Nagel M., Hany R., Lippert T., Molberg M., Nüesch F. A. and Rentsch D., *Macromol. Chem. Phys.*, **208** (2007) 277.

[7] Fardel R., Feurer P., Lippert T., Nagel M., Nüesch F. A. and Wokaun A., *Appl. Surf. Sci.*, **254** (2007) 1332.

[8] Karnakis D. M., Lippert T., Ichinose N., Kawanishi S. and Fukumura H., *Appl. Surf. Sci.*, **127-129** (1998) 781.

[9] Bonse J., Solis J., Urech L., Lippert T. and Wokaun A., *Appl. Surf. Sci.*, **253** (2007) 7787.

[10] Mito T., Tsujita T., Masuhara H., Hayashi N. and Suzuki K., *Jpn. J. Appl. Phys.*, **40** (2001) 805.

[11] Doraiswamy A., Narayan R. J., Lippert T., Urech L., Wokaun A., Nagel M., Hopp B., Dinescu M., Modi R., Auyeung R. C. Y. and Chrisey D. B., *Appl. Surf. Sci.*, **252** (2006) 4743.

[12] Xu J., Liu J., Cui D., Gerhold M., Wang A. Y., Nagel M. and Lippert T., *Nanotechnology*, **18** (2007) 025403.

[13] Fardel R., Nagel M., Nüesch F., Lippert T. and Wokaun A., *Appl. Phys. Lett.*, **91** (2007) 061103.

[14] Serra P., Colina M., Fernández-Pradas J. M., Sevilla L. and Morenza J. L., *Appl. Phys. Lett.*, **85** (2004) 1639.

[15] Hopp B., Smausz T., Antal Zs., Kresz N., Bor Zs. and Chrisey D., *J. Appl. Phys.*, **96** (2004) 3478.

[16] Toet D., Thompson M. O., Smith P. M. and Sigmon T. W., *Appl. Phys. Lett.*, **74** (1999) 2170.

[17] Kattamis N. T., Purnick P. E., Weiss R. and Arnold C. B., *Appl. Phys. Lett.*, **91** (2007) 171120.

[18] Bähnisch R., Gross W. and Menschig A., *Microelectron. Eng.*, **50** (2000) 541.

[19] Bera S., Sabbah A. J., Yarbrough J. M., Allen C. G., Winters B., Durfee C. G. and Squier J. A., *Appl. Opt.*, **46** (2007) 4650.

[20] Papakonstantinou P., Vainos N. A. and Fotakis C., *Appl. Surf. Sci.*, **151** (1999) 159.

[21] Zergioti I., Papazoglou D. G., Karaiskou A., Fotakis C., Gamaly E. and Rode A., *Appl. Surf. Sci.*, **208-209** (2003) 177.

[22] Brodeur A. and Chin S. L., *J. Opt. Soc. Am. B*, **16** (1999) 637.

[23] Nagura C., Suda A., Kawano H., Obara M. and Midorikawa K., *Appl. Opt.*, **41** (2002) 3735.

[24] Hare D. E., Franken J. and Dlott D. D., *J. Appl. Phys.*, **77** (1995) 5950.