Laser-Induced Backward Transfer of Monolayer Graphene

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Abstract

Laser-induced backward transfer (LIBT) has been demonstrated as a viable technique for precise, localised deposition of microscale regions of graphene. Single femtosecond laser pulses, shaped spatially using a digital micromirror device (DMD), were incident on a pre-prepared sample of graphene-coated nickel (the donor substrate) through a transparent glass receiver substrate. Under optimal laser exposure conditions, and in a low-pressure gas environment, circular regions of graphene with approximately 30 µm diameter were successfully transferred from the donor to the receiver substrate as confirmed by optical and electron microscopy and Raman spectroscopy. The hypothesis that rapid thermal expansion of the nickel could drive the transfer process is explored and is shown to be plausible through some simple calculations. This LIBT technique for transfer of this archetypal 2D material has many potential applications in photonic and MEMS device fabrication.

**Keywords:** Femtosecond, Laser, Transfer, Graphene, 2D Materials, DMD,

1. Introduction

Graphene and other 2D materials are of significant interest because their structure confines electron and phonon transport leading to properties that differ from bulk material of the same composition. For photonic devices [1] these materials potentially offer the ultimate in miniaturisation (single atomic layer structures), the possibility for novel optical and electronic properties, and even tuneability of these properties (e.g. by electric fields, straining or doping) [2, 3]. Currently the preferred method for production of 2D materials is growth via chemical vapor deposition (CVD), which can yield large-area monolayer coatings but is typically restricted to growth on particular catalytic surfaces. Integration of 2D materials into devices is then a complex process requiring many steps, such as transfer from the growth substrate to the device substrate via a polymeric intermediary overlayer, application of lithographic masking layers and chemical etching [4]. Here, we demonstrate a localised transfer method that allows 2D materials to be precisely and rapidly cut to shape and deposited directly onto the end device in a single-step process. This has the potential to radically lower fabrication time and costs, allowing a new class of photonic devices to emerge, based on 2D materials.

The CVD process is suitable for production of many allotropes of carbon such as nanotubes [5], nanowalls [6], and nanodiamond [7] depending upon the precise processing conditions used. As mentioned, CVD is currently the preferred method for production of large-area graphene. This is itself a wide topic of research [8], ranging from roll-to-roll scale production of polycrystalline graphene [9], to growth of wafer-scale single crystal graphene on copper and germanium [10]. In grossly simplified terms, the process begins with gas phase precursors such as CH4 which undergo reactions at high temperature and in proximity to a catalytic surface such as copper. Carbon species from the precursor are then adsorbed onto the surface where they can combine to form a graphene layer. As the graphene layer grows the area of exposed copper reduces and so the process is self-limiting, resulting in large-area, monolayer graphene.

In order to fabricate a CVD graphene-based device the graphene will typically need to be transferred to another substrate (a simple wet-chemistry approach for this is described in section 2.1). Additionally, it is usually necessary to localise the graphene to specific regions of the device. This can be achieved using lithographic masking and etching but requires many costly and time-consuming processing steps. In contrast, the method presented here achieves localisation of the graphene (and transfer from an intermediate substrate) in a single processing step.

The localised transfer method adopted in this work is a form of laser-induced transfer (LIT) in which the shape of the focussed laser spot defines the region of material transfer [11]. Here, the shape of the laser spot is controlled using a digital micromirror device (DMD) [12]; details of the DMD operation are provided in section 2.3. A brief note on terminology; it is common to refer to the material that is to be transferred as the ‘donor’, the support substrate for the donor is the ‘carrier’, and the substrate upon which the material is to be deposited as the ‘receiver’. These names will be used throughout, please refer to Fig. 2 for further clarification.

Several variants of the LIT process have been demonstrated in the literature; a key distinguishing feature is whether material transfer is in the same direction as laser propagation (laser-induced forward transfer, LIFT [13]) or in the reverse direction (laser-induced backward transfer, LIBT [14]). This work uses LIBT because it places fewer constraints on the thickness and composition of the initial support substrate (the carrier), making direct transfer potentially feasible from the catalytic substrate used for CVD growth. Expanding this point for the specific case of graphene; a copper carrier substrate that is thin enough to facilitate LIFT is likely to be unable to withstand the high temperature conditions that are required during the CVD growth process. Indeed, we have observed reflow and terracing of copper CVD growth substrates that results in surface undulations that are not amenable to laser focussing or successful laser transfer (see supplemental data).

Thicker solid films are routinely transferred via LIFT [11, 13] and liquid phase transfer of materials in solution is also readily achieved (e.g. graphene oxide [15] and carbon nanofibers [16]). For solid-phase, nanostructured, carbon allotropes, LIFT has been shown to be effective in transferring complexes of single-walled carbon nanotubes [17] (assisted by use of a triazene-based dynamic release layer, DRL) and hybrid carbon nanowall structures [18] (without the use of a DRL).

Turning our attention to 2D materials, localised transfer of monolayer graphene (although with a PMMA backing layer) has previously been demonstrated using both laser-induced pattern transfer (LIPT) [19] and LIFT [20]. Unfortunately, in many applications the PMMA layer that remains attached to the transferred graphene will prevent electrical or optical coupling and may not be readily removed by etching if, for example, it is trapped between the graphene and the device substrate. The authors of [20] claim that the mechanism for LIFT (without a DRL) is partial ablation of, and gas formation from, the transferred material itself; and that LIFT of monolayer graphene is, therefore, not possible without the use of a DRL. Contrary to this, blister-based LIFT [21] has demonstrated transfer of 2D materials such as MoSe2 and MoS2 (without a DRL). Instead the laser causes a gas filled bubble to form within the metal carrier and it is the rapid acceleration of the carrier surface that drives the transfer process. More recently, this blister-based method has been used to transfer crumpled fragments of CVD grown graphene [22] (which had previously been transferred to the donor via wet chemistry). Monolayer graphene LIFT of superior quality has also been achieved in [23] without using the blister method (but once again using wet chemistry to transfer the graphene onto the donor).

Whilst LIBT has previously been used for transfer of thin films (and was found to outperform LIFT) [24] we believe that this work is the first that demonstrates LIBT of monolayer graphene (or 2D materials in general). In this work, we also use wet chemistry to apply the graphene donor to the carrier substrate, however, we believe that only the LIBT method has the potential to overcome this limitation (by allowing the use of thicker carrier substrates) facilitating transfer direct from the CVD growth substrate thus making it an attractive technique for further study.

Summarising the main aspects of this work: We have demonstrated that laser-induced transfer of graphene from a flat nickel carrier substrate, onto a glass receiver is possible. We have explained that LIBT is a more favourable approach than LIFT since it has greater potential to allow transfer of graphene and other 2D materials directly from their growth substrates. Theoretical calculations are shown that put forward rapid thermal expansion of the carrier as a feasible mechanism for LIBT. We find that attempts to transfer graphene under atmospheric conditions results in break-up of the graphene, whilst in a low-pressure gas environment the profile imparted by the laser beam shape is retained. In this preliminary work the properties of the graphene are partially degraded during transfer, however, we predict that it will be possible to resolve this difficulty through improvements to the laser fluence control and uniformity.

1. Material and Methods
   1. Donor and Receiver Preparation

The donor material selected for these laser transfer experiments was monolayer graphene, grown on copper via chemical vapour deposition (CVD). The monolayer graphene synthesis was conducted using a low-pressure chemical vapor deposition process, as described in [25]. The growth substrates were 25 µm thick copper foils (Alfa Aesar, 99.999 % purity).

As will be discussed in section 3.5, although potentially feasible, direct transfer from the CVD growth substrate was not achieved and so here (prior to laser transfer) the graphene was transferred to the carrier substrate as follows: Post-synthesis a poly (methyl methacrylate) support layer was deposited onto the graphene from solution (PMMA 495K diluted to 2% in Anisole). The copper foil was then etched away using FeCl3. After multiple rinses in deionised water, the floating-film transfer technique was used to transfer the graphene-PMMA stack onto the carrier substrate (graphene side down). The carrier was a 1 mm thick quartz slide with a 50 nm thick layer of polycrystalline nickel (Ni) on the upper surface. The PMMA support layer was then dissolved using hot acetone. The resulting graphene-nickel-quartz donor was then rinsed in isopropanol and blow dried in nitrogen. The receiving substrate (the receiver) was a 170 µm thick, fused silica cover glass.

* 1. Laser Induced Backwards Transfer

The laser used was a Coherent Mira 900 Ti-Sapphire oscillator with a Legend-F-HE chirped pulse amplifier, providing pulse energy of up to 1 mJ at a centre wavelength of 800 nm and with a pulse duration of approximately 190 fs. The laser beam path incorporated computer-controlled pulse energy attenuation using motorised variable neutral density filters and beam shaping using a π-Shaper 6\_6 which converted the Gaussian intensity profile produced by the laser into a ’top-hat’ beam with uniform spatial intensity. The laser beam was introduced (via a beam-splitter) into a microscope imaging system, which used a 50x Mitutoyo Plan Apo NIR objective (NA = 0.42) and included a CMOS camera for alignment and monitoring purposes. The experimental apparatus is illustrated in Fig. 1.



Fig. .

Schematic diagram providing an overview of the experiment configuration.

Fig. 2 shows a more detailed view of the donor and receiver in order to illustrate the key steps in the LIBT process. This shows that in order to be absorbed in the carrier, the laser light (shaped by the DMD, see section 2.3) must first pass through the receiver (silica in this case) and the donor material (the graphene). In practice the donor and receiver were held in physical contact by constant pressure exerted by a mechanical spring, however, the inevitable presence of dust meant that the separation between the donor and receiver was estimated to vary in the range 1 – 10 µm. This estimate was based on the lateral size of dust particles that were observed by optical microscopy, with the assumption that their vertical height (and hence the donor-receiver separation) was in the same range. This separation is very small when it is considered that LIFT flyers (1.1 µm thick Bi2Se3 and 1.8 µm thick lead zirconate titanate) have been reported to travel intact for at least 500 µm [26].



Fig. .

Sequence of Illustrations showing the LIBT process. a) The set up before irradiation. b) During laser irradiation. c) Shows the flyer of 2D material during transfer (note that the transfer direction is opposite to the laser propagation direction). d) The situation after LIBT with the 2D material deposited onto the under-side of the receiver.

* 1. Digital Micromirror Device and Spatial Dithering

In this work a DMD was used as a binary spatial intensity filter [27], i.e. within the laser pulse duration each micro-mirror was essentially stationary in either the on or off position. The specific module used was a Texas Instruments DLP 3000 in which the micro-mirrors are actually arranged in a diagonal 2D array, however, our control electronics allowed static images with up to 854 x 480 pixels to be displayed on the DMD for beam shaping. The repeating structure of the DMD micro-mirrors acted as a 2D grating and so a screen was used to block unwanted diffracted orders as shown in Fig. 1. Each micro-mirror is approximately 7.6 µm x 7.6 µm in size but the microscope was arranged to project a de-magnified image of the DMD onto the sample, so that each mirror would theoretically illuminate a region on the donor that is 70 nm x 70 nm ±3 nm. Clearly this is well below the diffraction limit of our optical system (950 nm) which determines the actual lateral resolution achieved. Diffraction therefore tends to blend the light reflected from neighbouring micromirrors which benefits techniques such as spatial dithering described below. The DMD therefore provides precise digital control over transfer localisation, allowing irradiation and transfer of material with micron scale features.

In visible light projection systems that use DMDs, *temporal* dithering (or Pulse Width Modulation, PWM) is typically employed to allow graduated intensity control (overcoming the binary limitation of the mirror states). The short duration of the laser pulses means, however, that this approach is not possible here. In the results presented below *spatial* dithering of the binary DMD pixels was therefore used to achieve intermediate grey levels in the DMD image and hence to produce regions with differing fluence within a single laser pulse [28]. The Floyd-Steinberg dithering algorithm [29, 30] was used to convert from an 8-bit grayscale image to a binary image as required by the DMD. This is illustrated in Fig. 3 where the outer ring has an 8-bit grey level of 255 (i.e. full laser throughput) but the average level of the central spot is just 224 (i.e. partially attenuated throughput). Reasons for this strategy (using a high fluence ring) are discussed further in section 2.6 and in the discussions at the end of the paper. As mentioned above, since individual DMD mirrors illuminate a region of the sample that is less than 1 µm in size, diffraction tends to smooth out spatial variations in the resultant laser fluence arriving at the sample. This effect can be seen in inset c) of Fig. 3. which shows a measurement of the spatially modulated intensity profile of a white light beam reflected from the DMD, whilst it displays the pattern shown in insets a) and b).



Fig. .

Illustration of the concept of spatial dithering, showing how a DMD with binary (on or off) states can achieve grayscale intensity control. a) Example DMD image with spatial dithering to achieve higher intensity from the perimeter ring (8-bit grey level of 255, i.e. full intensity) than from the central spot (average grey level of 224, i.e. 88 % intensity). b) Magnified view showing the binary values for individual micro-mirrors. c) Measured intensity profile of white light that has been spatially modulated by reflection from the DMD (see supplemental data for more information).

* 1. Pressure Control

In previous research on LIFT, shadowgraphs have been used to reveal the presence of acoustic shockwaves and to measure their propagation speed under different initiation conditions [31]. Additionally, it has been shown that interaction between the flyer and the shockwave (during transfer) can cause flyer disintegration [32]. The authors of [33] also discus shockwaves reflected by the receiver and the fact that the air pressure plays a role in determining flyer velocity; concluding that intermediate pressures (between atmospheric and vacuum) may be beneficial. In sections 3.1 and 3.2 we present results of LIBT carried out both at atmospheric pressure and under partial vacuum. Our initial experiments were those carried out under atmospheric conditions and in these we observed breakup of the transferred material. Logically, when propelling a monolayer 2D material such as graphene through atmospheric pressure air (a viscous fluid) it will be subject to air resistance, turbulence and shockwaves. By lowering the air pressure these effects will be reduced and energy may be removed from the shockwaves (if these are present). Our later experiments therefore made use of a miniature vacuum chamber to lower the gas pressure; this was indeed found to benefit the transfer process.

For experiments that were carried out in low gas pressure conditions an additional sapphire window (1 mm thick) was present in the beam path between the microscope objective and the receiver. A dry, diaphragm, vacuum pump was used for initial evacuation only; the chamber was then kept sealed during experiments and was able to maintain a pressure of <1 mbar throughout. A diagram of the vacuum chamber is shown in Fig. 4.



Fig. .

a) Cutaway diagram of the miniature vacuum chamber (based on CF DN40 flanges) showing the spring mechanism that holds the donor and receiver in contact. The inset b) shows a photograph of the vacuum chamber.

* 1. Characterisation

To assess the quality and degree of intact transfer, Raman measurements were made using a Renishaw Invia Micro-Raman system with a 533 nm laser source and 2400 lines/mm grating. Scanning electron microscopy (SEM) was performed using the secondary electron detector in a Zeiss Evo 50 operated in variable-pressure mode.

* 1. Theory/Calculation

In the case of LIBT of graphene, the exact physical mechanism for the transfer process is not yet fully understood; in fact, it is likely that several effects act simultaneously. Although we acknowledge the possible contribution of other mechanisms, we have adopted as a working hypothesis the theory that the laser causes rapid thermal expansion in the carrier, providing sufficient momentum to locally eject donor material and hence transfer it to the receiver. We refer to this mechanism as the ‘piston effect’.

A greatly simplified calculation of the transfer of energy from the laser pulse to the carrier material was made as a first order test of the feasibility of this hypothesis. This calculation assumes that the laser intensity is spatially uniform at the carrier surface and that the pulse has a Gaussian temporal profile (*τFWHM* = 190 fs). (For simplicity, absorption and reflection of the receiver and donor material are ignored). The Beer-Lambert law is then used to calculate laser intensity within the carrier as a function of depth below the surface (*Z*) and time (*t*), see Fig. 5. This simply applies an exponential decay of laser intensity with penetration depth below the surface of the carrier. An attenuation coefficient α = 4πκ/λ is assumed, where κ is the extinction coefficient (the imaginary part of the refractive index, which for Ni is 4.89 at 800 nm [34]). The spectral bandwidth of the laser (6 nm FWHM) is ignored so all light is assumed to be at the centre wavelength *λ* = 800 nm. For Ni, reflectivity at the surface of the carrier is assumed to be *R* = 0.74 (calculated using the Fresnel equations, assuming normal incidence, with refractive index *n* = 2.22 [34]).



Fig. .

Image plot of laser intensity within the carrier (Ni) as a function of depth below the surface (vertical axis) and time (horizontal axis).

For this analysis, the assumption is made that all attenuated laser energy is converted directly to heat within the carrier bulk; calculations of temperature change and thermal expansion, as can be found in many physics textbooks, e.g. [35], then follow. Using the heat capacity of Ni, which is a function of temperature [36] and assuming that the Ni is initially at room temperature we can calculate the change of temperature within the Ni during the laser pulse (Fig. 6.). Note that processes such as thermal conduction, ionisation and two photon absorption are all ignored and that for the fluence used in these calculations (30 mJ/cm2, the same fluence used in the experimental results) the melting point of Ni (1728 K) is not exceeded.



Fig. .

Image plot showing the calculated temperature profile in the Ni carrier as a function of penetration depth (vertical axis) and time (horizontal axis) when subjected to a 190 fs pulse with fluence of 30 mJ/cm2.

The final step in this simplified model is to assume linear thermal expansion within the carrier in order to estimate the displacement of the carrier surface as a function of time. The surface velocity and acceleration may then be calculated by numerical differentiation as shown in Fig. 7. Note that the dip in surface acceleration approximately 50 fs before the peak of the laser pulse is a genuine feature that arises from a large peak in the temperature-dependent heat capacity of Ni that occurs between 600 and 700 K.



Fig. .

a) Surface displacement, b) velocity and c) acceleration calculated for a Ni carrier as a function of time when subjected to a 190 fs pulse with fluence of 30 mJ/cm2.

The estimate of peak surface velocity (1219 m/s) falls between experimentally measured LIBT flyer velocities (6 - 20 m/s [37]) and the speed of sound in bulk Ni (6040 m/s [38]). The apparently large discrepancy between peak surface velocity and experimentally measured flyer velocity is to be expected: Neglected factors such as thermal conduction will tend to dissipate energy, reducing the magnitude of the thermal expansion effect. The flyers observed in [37] have considerably higher mass than would be the case for a graphene donor. Furthermore, flyers are not necessarily ejected with the maximum surface velocity and air resistance (when not operating under vacuum) can further slow their flight. Despite this, flyer velocities of almost 1000 m/s have been observed in LIFT experiments [39].

At the negative peak in acceleration, a single carbon atom on the Ni surface would require an adhesion force of at least 178 pN in order to remain in contact with the surface (*F = ma*). The binding energy between graphene and a Ni (111) surface is estimated using density functional theory to be 91 meV and to act over a distance of approximately 2 Å [40]. This equates roughly to a force of just 72 pN which we take as an upper bound since the binding energy is likely to be lower for the polycrystalline Ni used in our experimental work. In this calculation (for a fluence of 30 mJ/cm2) we therefore expect the surface acceleration of the Ni to exert a force on the graphene that is sufficient to overcome its surface binding forces; furthermore we predict that the threshold fluence to overcome surface binding could be as low as 11 mJ/cm2. In contrast, the carbon-carbon bonds within the graphene plane are approximately 1.42 Å in length and have a bond energy of 4.93 eV [41], equating to a force of 5562 pN. This simple calculation consequently predicts that these in-plane carbon-carbon bonds will not be broken by the surface acceleration; however, note that we have not considered shearing forces which could make this more likely.

In conclusion, whilst the calculations above are highly simplistic and include many approximations they demonstrate that laser energy sufficient to overcome the graphene-Ni binding can be deposited into the carrier. They also show that rapid thermal expansion of the carrier is a feasible mechanism for kinetic energy transfer to the donor, and that this is sufficient for subsequent donor detachment. Furthermore, it is highlighted that detachment of graphene from the Ni carrier (overcoming Van der Waals forces) requires considerably less energy (91 meV per bond) than rupture of the graphene structure (i.e. breaking of the in-plane carbon-carbon bonds takes 4.93 eV per bond). For intact transfer of graphene, it is necessary to break carbon-carbon bonds at the perimeter of the transferred region only. Breaking carbon-carbon bonds within the transferred region would destroy the graphene. This explains the effectiveness of the spatial light modulation pattern described in section 2.3 (high fluence ring with lower fluence centre circle).

1. Results and Discussion
   1. LIBT under atmospheric conditions

Fig. 8. a) shows an optical microscope image (taken using a 100x objective) of a laser- irradiated region of the donor. This consists of monolayer graphene that was applied (via a polymeric overlayer) onto a 50 nm thick layer of Ni on a quartz substrate. A circular mask was defined on the DMD and laser fluence was adjusted (to approximately 30 mJ/cm2) in order to remove the graphene whilst leaving the Ni layer intact. The contrast of the (originally colour) image has been enhanced in order to show more clearly the laser-induced change in appearance. The region of graphene removal can be seen as a circle of slightly lighter colour near the centre of the image. Dark specks are dust contamination that is present on the surface of the graphene and is also assumed to be trapped between the graphene and Ni. Note that a torn fringe of graphene is also visible around the perimeter of the hole (indicated by the arrow).

In Fig. 8. b) two images recorded via the micro-Raman system are combined. The red dashed circles highlight regions that have been subjected to low fluence laser irradiation (30-75 mJ/cm2, left to right) whilst on the left of the image several examples of higher laser fluence (approximately 250 mJ/cm2) are clearly visible. The green spots labelled L and G respectively indicate the position of Raman measurements inside the laser irradiated region and outside (where the graphene coating remains). These Raman spectra are plotted in Fig. 8. c); the upper (blue) line confirms that peaks characteristic of graphene are present outside of the laser irradiated region (location G) whilst the lower (red) line confirms that they are absent at location L, after irradiation at 30 mJ/cm2. The characteristic peaks of interest are commonly referred to as the G and 2D peaks marked at 1583 cm‑1 and 2666 cm‑1 respectively and additionally of interest is the D peak (near 1350 cm‑1) the presence of which can indicate defects in the graphene structure. (Note that for the particular sample shown in Fig. 8. the 2D peak appears to be shifted to lower wavenumbers, perhaps due to interaction with the Ni. It is more typical for the 2D peak of graphene to be near 2680 cm‑1 as was the case for the other samples presented below).



Fig. .

a) Optical microscope image showing a laser-irradiated region of the donor. Image contrast has been enhanced in order to show the laser-induced change in appearance. The red dotted line is a guide for the eye showing the perimeter of the laser-irradiated region. b) Optical microscope images of the donor taken using the micro-Raman system, the red dotted circles indicate positions subjected to low fluence laser irradiation. The green spots at G and L indicate the positions of the Raman measurements. c) Raman spectra, upper line (blue) was recorded at position G and show peaks associated with monolayer graphene, the lower line (yellow) corresponds to the laser-irradiated region at position L where the graphene peaks are absent.

Fig. 8. demonstrated that graphene can be removed from the donor under atmospheric conditions, however, only small fragments of graphene can be found on the receiver even if it is held in close contact with the donor. Fig. 9. shows Raman spectra with characteristic peaks confirming that fragments of material found on the receiver substrate are indeed graphene. Graphene fragments appeared on the receiver in the vicinity of LIBT experiments but were often spread over an area that considerably exceeded the size of the irradiated region (i.e. deposition was poorly localised).



Fig. .

a) and b) Optical microscope observations of the receiver (with enhanced contrast) showing the location of Raman measurements (position 020 and 021 respectively). c) Representative Raman spectra for fragments of graphene transferred via LIBT to a fused silica receiver. Upper (blue) line corresponds to position 020 shown in a) and lower (yellow) line is for position 021 shown in b).

SEM imaging reveals that the graphene fragments sometimes lie flat on the receiving substrate and sometimes curl up (see Fig. 10.). Optical attenuation and Raman signal are greatly enhanced at locations where the graphene scrolls or folds. As shown in inset Fig. 10. c) the fragments often appear to be pushed towards the periphery of the laser irradiated region due perhaps to a force acting radially outwards such as thermal expansion of the air; this was therefore one of the motivations for the next set of experiments performed with reduced gas pressure.

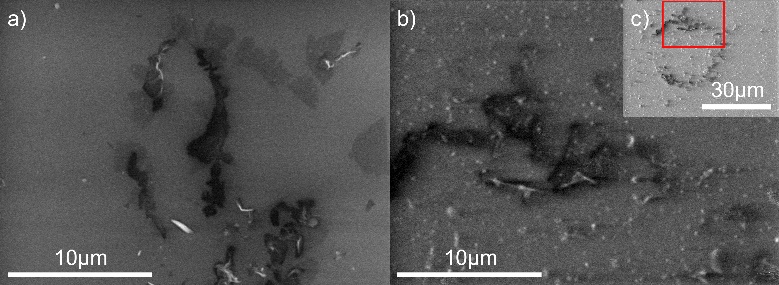


Fig. .

SEM images of graphene fragments transferred onto the fused silica receiver by LIBT at atmospheric pressure. a) and b) are at the same magnification and show examples of the resultant deposition when the laser irradiates a circular region, 30 µm in diameter. c) Is at lower magnification and shows the context of the region featured in b).

* 1. LIBT in a low-pressure gas environment

In line with previous observations of improved LIFT performance at reduced environmental pressure such as [42] it was hypothesised that the laser-induced motion of the carrier substrate could create an acoustic shock wave in the gas between the carrier and receiver or that the laser irradiation could simply lead to rapid thermal expansion of the gas or even to ionisation and electrostatic repulsion. For this reason, further experiments were carried out under conditions of partial vacuum (the gas filling the chamber was air but a pressure of <1 mbar was maintained throughout the experiment).

Fig. 11. Shows optical microscope images of the donor a) where a circular area of graphene has been removed by the laser (perceived via the lighter colour) and the corresponding region on the receiver b) where a circular feature of very similar size and shape is observed. In b) it is the edge of the graphene region that is most clearly seen (as a darker line) perhaps due to additional scattering caused by particles ejected from the ring of higher laser fluence. The optical microscope results suggest that in contrast with the fragmentation that occurs at atmospheric pressure; in a low gas pressure environment, intact LIBT of the graphene has been achieved.



Fig. .

Optical microscope images of a) the Ni donor showing removal of graphene and b) the receiver showing intact transfer of the graphene. The blue dotted curves have been added as a guide for the eye, to help identify the circular region.

SEM imaging of the receiver was challenging due to surface charging of the fused silica substrate, however, Fig. 12. a) shows an image of the same region of the receiver as featured in Fig. 11. b). The accelerating potential was reduced to 5 kV to minimise damage to the sample and variable pressure mode was used to mitigate charging. The DMD image used in this experiment was as shown in Fig. 3. with the outer rim of the laser spot receiving the full 30 mJ/cm2 fluence, whilst the central circle is attenuated to an average value of approximately 26 mJ/cm2. There is perhaps evidence for increased scattering of graphene fragments from the rim region, however, this approach does seem to have achieved detachment and transfer of the complete circle of graphene to the receiver. Brighter specks with a circular appearance are likely to be particles of Ni that have been ejected in a molten state due to localised hotspots in fluence. These were observed in very large numbers when the laser fluence is increased as shown in Fig. 12. b).

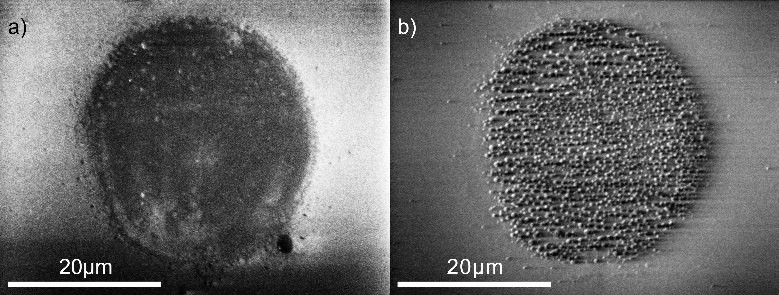


Fig. .

a) SEM image of graphene transferred to the receiver substrate (the same location as shown in Fig. 11. b)). b) At higher fluence (130 mJ/cm2) material in spherical beads is deposited, likely to be Ni that was molten during transfer.

Confirmation that the material transferred to the receiver is in fact graphene was obtained by taking multiple Raman spectra at different positions across the circular feature. The signal from an unmodified part of the receiver, outside of the laser irradiated region, was taken as the background and was subtracted from all other spectra. In Fig. 13. a) the colour markers indicate the approximate position of the Raman laser during each spectral acquisition. Those spectra in Fig. 13. b) that correspond to the circular feature clearly contain characteristic peaks that indicate the presence of graphene. Outside of the circular feature these characteristic peaks disappear.

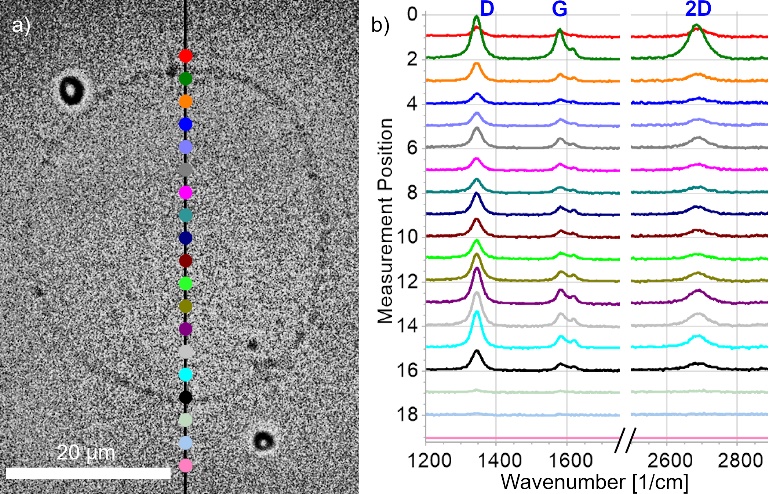


Fig. .

a) Optical microscope image of graphene transferred to the receiver (same data as Fig. 11. b), contrast enhanced and converted to monochrome to show colour markers indicating the approximate locations of Raman measurements). b) Raman spectra recorded at multiple positions across the transferred graphene spot (blue text labels indicate the peak assignment).

* 1. DMD Spatial Dithering

The theoretical calculations in section 2.6 highlight that the force required to break the graphene’s in-plane carbon-carbon bonds (5562 pN) is significantly higher than that needed to detach the graphene from the substrate (overcoming Van der Waals forces, 72 pN). In section 2.3 it was explained that spatial dithering of the DMD image can be used to produce a circular laser pattern surrounded by a ring with higher fluence. The results presented in Fig. 11. - Fig. 13. were all obtained using this beam shape. This intensity profile was selected with the intention that the higher fluence at the rim of the circle would provide additional energy needed to break the graphene’s in-plane carbon-carbon bonds, aiding release of the graphene from the donor. To-date it has not been possible to reproduce the intact transfer of graphene without the use of a higher fluence outer ring. Whilst it is not yet possible to rule-out transfer with a uniform circular intensity profile, this may require far higher precision of fluence control. Logically, with uniform intensity, if the laser fluence is high enough to break the carbon-carbon bonds at the rim of the transfer region then it will also be sufficient to break bonds within that region – leading to breakup of the 2D material.

* 1. Quality of the transferred graphene

When comparing the graphene deposited under atmospheric conditions with that deposited under low pressure conditions there are several key differences. Most strikingly, with low gas pressure, intact transfer of the complete irradiated region has been achieved, whilst under atmospheric conditions the graphene breaks into small fragments. Clearly, intact transfer with the region of deposition being defined by the laser beam profile is highly desirable, however, the Raman data indicates that the quality of graphene transferred to the receiver is higher in the case of atmospheric transfer. This is most obviously shown by the presence of a large D peak signal near 1350 cm-1 in Fig. 13. which is not evident in Fig. 9. This may at first seem counter-intuitive since if the graphene were at elevated temperature one might expect a higher rate of reaction (eg. with oxygen) and therefore more degradation of the graphene in the higher-pressure environment. However, within the extremely short duration of the laser pulse (190 fs) we expect the heat transfer from the Ni to the graphene to be minimal (indeed this was neglected in the calculations presented in section 2.6). One possible explanation could therefore be a difference in the transfer mechanism, i.e. whilst the thermal expansion ‘piston effect’ described in section 2.6 may apply to partial vacuum transfer, perhaps under atmospheric conditions rapid expansion of the air dominates. Under atmospheric conditions graphene that is ‘blown’ onto the receiver interacts primarily with rapidly expanding (and therefore relatively cooler) gas, and as a result retains much of its atomic structure but loses its shape, perhaps due to break-up in the turbulent air flow. Conversely, under partial vacuum conditions the transfer process may be driven by direct interaction between the graphene and the expanding Ni carrier (which is at high temperature). Under this process the transfer region is able to retain its shape but for this mechanism there seems to be a greater chance that the laser can cause damage to bonds within the transferred graphene. Using the calculations presented in section 2.6, the change in fluence from the rim (30 mJ/cm2) to the central circle (26 mJ/cm2) results in a difference in the peak temperature achieved on the Ni surface of over 165 K. Although the surface acceleration in the 30 mJ/cm2 region was predicted to be inadequate to break the in-plane carbon-carbon bonds it is believed that the additional temperature of the carrier (or even direct absorption of the laser) may mean that the threshold for vaporisation/ablation of the graphene is exceeded in the rim region but not met in the central circle.

The D peaks observed in Fig. 13 are perhaps therefore an indication that the laser fluence in the centre of the laser spot is still slightly too high or is insufficiently uniform. Spikes in fluence (spatially) could lead to unintentional breaking of carbon-carbon bonds within the circular transferred region. This could cause tearing and edge-type defects, distributed across the transferred graphene, which would exhibit the characteristic D peak [43]. Our existing laser system suffers some aberrations meaning that even after the π-shaper the beam uniformity is sub-optimal. It is hoped that enhancements to the precision of laser fluence control and beam shaping can be achieved (perhaps without the requirement for spatial dithering) and that these will allow larger contrast between the irradiation of the ring and circular region and for better spatial uniformity. We believe that these will be the key factors required to improve the quality of graphene that is transferred via the LIBT mechanism.

* 1. Prospects for use as an industrial process

In the results presented above the graphene was first grown via CVD onto copper, then applied via a polymeric overlayer onto the Ni carrier, prior to the localised LIBT transfer. The polymeric transfer process (as described in section 2.1) is suitable for large areas (centimetre scale) whilst the LIBT process allows deposition of shaped regions that are 10s of microns in size. In the possible end application (fabrication of photonic devices based on 2D materials) if graphene is deposited onto the device via CVD growth or via polymeric layer transfer then many subsequent lithographic steps (deposition of resist layers, exposure of a mask, chemical etching, etc) will be required. Conversely, in the laser transfer method presented here, 2D material with the shape required for device functionality can be deposited in a single step. Aside from reducing wastage of the 2D material and lithographic processing chemicals (particularly solvents) this also potentially allows greater freedom in the device design, which might otherwise be constrained by requirements of the lithographic process.

In other laser transfer methods mentioned in section 1, such as LIFT and blister-based LIFT, the carrier is positioned between the laser and the donor. If a DRL is used, or if partial ablation of the donor is permitted, then it is possible to use a carrier that is transparent to the laser light, however, typically the carrier must be strongly absorbing. This has the advantage that the carrier provides the donor with some protection from direct damage by the laser. The LIFT configuration, therefore, requires absorbing carriers (such as metals) to be very thin, which typically prevents them from also serving as the CVD growth substrate. In contrast, the LIBT process has the potential to allow transfer of 2D materials direct from their CVD growth substrates (eliminating the need for the polymeric overlayer transfer step in donor preparation). This would greatly strengthen the case for adopting LIBT as an industrial process for device fabrication. Initial attempts at direct transfer from thin-film copper CVD growth substrates have proved unsuccessful because the high temperatures that are required during graphene growth cause re-flow of the copper surface which takes on an undulating shape and leads to spatial variations in laser fluence at the carrier. Nevertheless, LIBT direct from the CVD growth substrates remains an active line of future research with possible solutions including CVD growth of graphene onto Ni, platinum, or other high temperature metals or CVD growth onto thicker single crystal copper specimens.

1. Conclusion

We have demonstrated that it is possible to transfer monolayer graphene from a Ni carrier substrate to a fused silica receiver substrate using LIBT with a femtosecond laser source. To our knowledge, this work is the first to demonstrate LIBT of graphene (or, in fact, any 2D material). At atmospheric pressure the graphene breaks into fragments during transfer but in a low-pressure gas environment circles of graphene approximately 30 µm in diameter were transferred intact. The presence of atmospheric pressure gas is thought to result in viscous drag, turbulence and pressure shockwaves (as reported in prior literature) that cause the fragmentation of the graphene flyer during transfer.

A DMD was used to define the size, shape and position of the graphene deposit and, furthermore, spatial dithering on the DMD image was used to achieve fine control over the spatial distribution of fluence within a single laser pulse. This allowed higher laser fluence to be delivered at the perimeter of the transfer region, thus providing the additional energy needed to break the in-plane carbon-carbon bonds. Under the optical microscope and SEM, the transferred graphene appears to uniformly cover the entire selected region, however, Raman measurements contained elevated D peaks, indicating that the quality of the transferred graphene was degraded, perhaps due to the introduction of micro-tearing, through reaction with the atmosphere during the transfer process or due to localised peaks in laser fluence within the transfer region.

For LIBT to be successful in fabrication of devices based on 2D materials the process must be further refined in order to improve the quality of the transferred material. Nevertheless, laser transfer has the potential to eliminate many time-consuming lithographic processing steps and allow precise, direct application of 2D materials, with complex shapes, to specific locations on the device. Significant further gains in efficiency can be obtained if transfer direct from the CVD growth substrate can be achieved; we predict that this is more likely to be feasible for LIBT than for LIFT, since LIBT allows the use of thicker carriers which are robust against the high temperatures used in the CVD process.

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CRediT authorship contribution statement

**Matthew Praeger:** Methodology, Software, Formal Analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Symeon Papazoglou:** Methodology. **Amaia Pesquera:** Resources, Writing – review & editing. **Amaia Zurutuza:** Resources, Writing – review & editing. **Adi Levi:** Resources. **Doron Naveh:** Resources, Writing – review & editing. **Ioanna Zergioti:** Conceptualization, Project Administration, Writing – review & editing, Funding acquisition. **Robert W. Eason:** Methodology, Supervision, Writing – review & editing, Project Administration, Funding acquisition. **Ben Mills:** Methodology, Resources, Supervision, Writing – review & editing, Project Administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2020.147488. Data supporting this study are openly available from the University of Southampton repository at <https://doi.org/10.5258/SOTON/D1502>.

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