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Laser induced forward transfer of soft materials

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Abstract

A strong research effort is presently aimed at patterning methodologies for obtaining controlled defined micrometric polymeric structures for a wide range of applications, including electronics, optoelectronics, sensors, medicine etc. Lasers have been identified as appropriate tools for processing of different materials, such as ceramics and metals, but also for soft, easily damageable materials (biological compounds and polymers). In this work we study the dynamics of laser induced forward transfer (LIFT) with a gap between the donor and the receiver substrates, which is the basis for possible applications that require multilayer depositions with high spatial resolution.

Keywords: µ-beads, LIFT, shadowgraphy

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The precise positioning of different materials, including metals, oxides, and biomolecules (i.e. proteins, DNA, cells, tissue) is an important step for the advancement of many applications. One technique that has received extensive attention recently is laser induced forward transfer (LIFT). LIFT is a versatile deposition technique where the material of interest is transferred by the laser beam from a transparent support or donor onto an appropriate substrate or receiver. In particular, this technique allows one to obtain high resolution patterns of materials which are defined by the shape of the laser beam.

In conventional LIFT the material to transfer is directly irradiated by the laser pulse, which in the case of metals may be acceptable. However, there is a great interest in printing complex materials such as light emitting polymers or biological materials which are transparent or even damaged by direct laser irradiation. To overcome these difficulties, an absorbing metallic layer is usually placed between the donor film and its support to absorb the laser pulse and to propel the intact donor layer [1–3]. These metallic sacrificial layers have many advantages (i.e. they are easy to deposit as thin films) but a major drawback is that debris, i.e. metal fragments, may be present in the transferred material, perhaps due to incomplete vaporization [4]. Furthermore, when the metallic layer is fully vaporized it leads to major heating of the layer to be transferred.

As an alternative to the metallic layers, suitable materials to be used as the sacrificial layer are photosensitive polymers, in particular triazene polymers (TP) [5], because they decompose upon UV laser irradiation into gaseous fragments which transfer the soft material, with a minimum thermal load, to a receiver [6, 7]. The use of a triazene polymer as dynamic release layer (DRL) has numerous advantages, i.e. (i) the triazene polymers have a very low ablation threshold of ∼25 mJ cm⁻² for 308 nm irradiation, which means that the transfer can be achieved with low thermal impact on the donor layer; (ii) no debris is detected, and (iii) a high absorption coefficient at the XeCl excimer laser wavelength [8–10]. The above specified advantages of the TP make them suitable for transferring a wide range of materials, such as organic light emitting diode pixels [11], living cells [12], nanocrystal quantum dots [13], thin metallic films [14], or polymer membranes [15].
In the above presented examples the transfer was carried out mostly with the receiver and the donor in contact, but this approach is difficult to apply for large area substrates or for successive multilayer depositions. Therefore, it is important to understand how the material is ejected from the support and transferred onto a substrate when the two supports are not in contact.

In a previous study [16] we have demonstrated that a clean transfer of polystyrene microbead pixels by the nanosecond LIFT technique is possible. The PS-µ bead pixel transfer was carried out onto Thermanox coverslips and the transfer was realized with the receiver and the donor substrates in contact.

In the present study we use a time resolved imaging technique [17, 18] to analyze the direct laser ejection of polystyrene microbead (PS-µ beads) pixels. We analyze the case when the laser transfer of PS-µ beads is achieved with different gaps between the donor and the receiver, in order to better understand the dynamics of the forward transfer of the material onto the substrate.

The polystyrene microbeads were chosen as study materials due to the large range of laser fluences for which they can be transferred as clean cut pixels (0.7–3 J cm⁻²), as compared to other polymer materials [15], while preserving their chemical composition intact. Microbeads of polystyrene, as well as of different materials, have been utilized in various fields of research, e.g. in optics, electronics, and biology. Examples of applications include biosensing [19], bioseparation [20], biomolecule screening [21], mask lithography [22] and as lens arrays allowing single step large area parallel processing [23–25].

2. Materials and methods

The pulsed UV XeCl laser beam (308 nm emission wavelength, 30 ns pulse length, 1 Hz repetition rate) is guided and focused on the donor substrate by an optical system to transfer PS microbead (8 µm in diameter) pixels (200 × 200 µm²) from the target (also called donor substrate) to the receiving surface. The laser fluence was varied from 80 mJ cm⁻² to 3.5 J cm⁻². For each laser pulse one polystyrene microbead pixel was obtained and several of them were arranged in a matrix of points.

A computer-controlled xyz translation stage allows the placement of both the target and receptor substrates with respect to the laser beam. The target and the receiver were kept at a distance ranging from 40 to 100 µm, while the laser irradiated the donor from the backside.

The experimental configuration for the LIFT process is depicted in figure 1.

The targets were prepared by spin coating the triazene polymer (thicknesses 100 nm) onto fused silica plates and then drop casting the PS-µ beads (8 µm in diameter).

Glass slides or Thermanox coverslips were used as receiver substrates and were cleaned prior to the experiments.

The transferred features by LIFT were morphologically investigated. The optical microscopy images were acquired with an Axiovert 200 Microscope coupled to a Carl Zeiss AxioCam MRm camera. The distribution of the PS-µ spheres on the receiving surface was investigated using a scanning electron microscope (SEM) operating at a voltage of 5 kV with an in-lens detector. The samples were coated with a 3 nm thin Pt film for conductivity.

For imaging the laser transfer process on a nanosecond timescale a pump–probe shadowgraphy setup was used.

A camera with a zoom objective was placed perpendicular to the pump excimer XeCl laser beam (parallel to the sample surface) with the focus at the ablation spot. Illumination was provided by the probe, i.e. a Nd:YAG laser (from Quantel Brilliant B, 5 ns pulse length) operating at the second harmonic (532 nm wavelength) pumping a rhodamine fluorescent dye in a cuvette placed on the camera axis on the opposite side of the sample. The delay between the pump and the probe pulse was obtained with a digital pulse/delay generator [18].

All measurements were performed under ambient pressure at room temperature. A single image frame was acquired for each laser pulse, using an integration time of 100 ns.

3. Results and discussion

3.1. Transfer characterization

A range of laser fluences in which well defined pixels are obtained exists for the case of donor and the receiver substrates in contact, as previously reported (0.71–3.5 J cm⁻²) [16]. An optical microscopy image of PS-µ bead pixels transferred at two different laser fluences with the donor layer and the receiving substrate in contact is shown in figure 2. The shape of the pixels is homogeneous, defect free and reproducible. However, this is not the case when the two substrates are separated by a gap.
Figure 3. Optical microscopy image of laser transferred PS-μ bead pixels at 1 J cm⁻² laser fluence with different distances between the target and the receiver. The scale bar is 200 μm.

The transfer distance was decreased gradually from 100 to 40 μm in order to assess the differences in shape and homogeneity of the transferred pixels (see figure 3).

In figure 3 each column corresponds to different distances between the target and the receiver support, i.e. the distance between the target and the receiver increases from 40 to 100 μm (from right to left). The shape of the transferred PS-μ bead pixels becomes more and more irreproducible, and for distances above 70 μm, at the applied laser fluence of 1 J cm⁻², only randomly spread beads are found on the receiver substrate (figure 3).

For a distance of 50 μm between the target and the receiver the laser fluence was additionally varied over a broad range (80 mJ cm⁻²–3.5 J cm⁻²) to verify whether it is possible to obtain a regular, debris-free transfer. An optical microscopy image of the deposited features at different laser fluences is shown in figure 4. All applied laser fluences for the transfer were investigated three times.

The images in figure 4 suggest that with increasing fluences, which are much higher than the fluence necessary to ablate the TP layer of 50 mJ cm⁻², the shape of the transferred pixels improves, although still not comparable to the transfer without a gap. For laser fluences up to 1 J cm⁻², only random beads are transferred on the receiving substrate (see figure 4). In the case of high laser fluences applied (i.e. up to 3.5 J cm⁻²), which lead to strong propulsion of the PS-μ beads, the transfer is still not homogeneous and reproducible. This may be due to reflection of the shockwave from the receiver substrate which may slow down the movement of the pixel towards the substrate, or even ‘destroy’ the pixel (as explained in section 3.2).

The target after ablation at different laser fluences is shown in figure 5(c). An inspection of the target after ablation at 1 J cm⁻² (figure 5(b)) supports the observation that the laser fluence was high enough to ‘cut’ a clean pixel from the target but that the pixel was probably destroyed by the shockwave. The edges of the ablated pixels are well defined and almost no beads remain inside the ablated pixels (figure 5(b)). The remaining beads in the target can be removed by a gentle stream of nitrogen.

At lower laser fluences i.e. 100–500 mJ cm⁻² (figures 5(a) and (c)) the fluence was not high enough for the complete removal and transfer of the PS-μ beads. Inside the ablated pixels (figure 5(a)) randomly distributed beads are still present.

In addition, the non-homogeneities that are present in the target (marked with arrows in the optical microscopy images figures 5(b) and (c)) are most probably due to the deposition method of the PS-μ beads on the TP coated fused silica substrate, which in our case was drop casting.

The SEM images (see figure 6) of some randomly selected beads on the substrate suggest that the morphology of the PS-μ beads is not changed as a result of the laser transfer.
3.2. Time resolved imaging

In order to understand the mechanisms that lead to the features observed in the deposited material, a series of side view images of the transfer process were acquired.

Figure 6. SEM micrograph of the surface morphology of the PS-µ beads transferred at 2 J cm⁻². The scale bar is 20 µm.

A sequence of pictures taken at 1 J cm⁻² with a 100 nm thick triazene polymer film is shown in figure 7. The receiver surface is on the left, while the laser pulse comes from the right. The distance between the donor and the receiver is adjusted by spacers to 100 µm.

Two features can be clearly distinguished in the images. The fast moving front (feature A in figure 7), which appears as a dark semicircle, is attributed to the shockwave caused by the temperature/pressure jump at the ablation spot, where a large amount of gas is released during the laser pulse [18]. The shockwave and its expansion are clearly visible after 200 ns. After 800 ns the shockwave is reflected by the receiver surface (denoted as B in figure 7). The third feature that appears (letter C in figure 7) is most probably formed by gaseous decomposition products from the TP [18]. The presence of this feature indicates a clean and debris-free (no TP in the deposited features) transfer by TP-DRL assisted LIFT. The ejection of the entire PS-µ bead layer is observed after 1000–1200 ns, with a clear separation of the layer from the substrate after 2400–2600 ns. The PS-µ bead layer clearly appears thicker than the thickness of the 8 µm bead layer as the CCD camera was most probably slightly tilted.

The ‘flyer’ (PS-µ bead pixel) is highly forward directed and keeps its cohesion for distances of about 30 µm, which explains why for larger distances, i.e. 100 µm, the PS-µ beads

Figure 7. Sequence of pictures taken at 1 J cm⁻² with a TP layer of 100 nm. The laser comes from the right, while the substrate is on the left. The time delays are indicated on the frames. The arrows indicate the features A, B and C which are described in section 3.2.
pixels do not reach the receiver surface. This may also be due to the reflection of the shockwave which slows down the movement of the flyer. These observations are also supported by the optical microscopy images of the deposited features shown in figures 3 and 4. The nanosecond-shadowgraphy images reveal that it is not possible to obtain well defined, homogeneous PS-µ bead pixels when a gap between the donor layer and the receiver is used.

4. Conclusions
Laser induced forward transfer provides a precise control over the location of a transferred material (PS-microbead pixels) for a set of well defined parameters. By using LIFT with the donor and the receiver substrates in contact, well defined pixels arrays are obtained.

In this work the LIFT-transfer of PS-µ beads was investigated by time resolved shadowgraphy. The transfer parameters reported in this study suggest that by maintaining a gap between the donor layer and the receiver substrate it is not possible to obtain pixels with well resolved edges for solid materials. Further studies will show whether it is possible to find a set of parameters which allow the transfer of solids when there is a gap between the donor and receiver substrates.

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