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Laser forward transfer using a sacrificial layer: Influence of the material properties

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Abstract

The deposition of metal and polymer patterns was achieved with a laser forward transfer method involving a sacrificial release layer. Aluminum, gelatine and methylcellulose pixels were precisely transferred from a donor to a receiver substrate using the UV-laser decomposition of an intermediate triazene polymer layer. The roughness and edge sharpness of the pixels are found to be very dependent on the transfer material. For aluminum, a thick layer of triazene has to be used to get a clean transfer, which remains unclear yet. The applied fluence as well as the triazene thickness are strongly interdependent on the mechanical properties of the transfer layer. This work endeavours some important aspects of the transfer mechanism, and opens the way to further investigations, which are necessary to get a clear understanding of the process.
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1. Introduction

Laser processing of materials is a very important class of methods that allow to remove, modify or deposit materials using the interaction with a laser beam. Several techniques have been developed for depositing materials with a laser. Pulsed laser deposition (PLD) allows to grow films of inorganic [1,2] or organic materials [3–6] on a substrate. Matrix-assisted pulsed laser evaporation (MAPLE) is used for depositing small molecules trapped in a frozen matrix of solvent [7,6]. A very promising method of precise deposition is the laser-induced forward transfer (LIFT) [8,9]. A transparent carrier is coated with the material to transfer and placed close to a receiver substrate. A laser pulse impinges through the donor substrate on a precise spot of the film and triggers its ablation and subsequent redeposition on the receiver.

Whereas this technique is readily applied to metal layers, it presents some limitations for sensitive materials such as polymers, since it will damage the latter by thermal load and photochemically triggered reactions. To avoid this, an intermediate layer can be used to absorb the laser. This sacrificial layer, also called dynamic release layer, must have a low ablation threshold and avoid excessive thermalization of the absorbed photons. A particularly well suited material is the triazene polymer (see Fig. 1). It decomposes upon laser irradiation into small gaseous fragments, providing the thrust for propelling the top layer. Moreover it has a very low ablation threshold (≈ 25 mJ/cm^2), meaning that transfer can be achieved with low thermal impact on sensitive materials [10–12].

The triazene polymer has been successfully used for the transfer of quantum dots [13], living cells embedded in a matrix [14] and recently, functional organic light-emitting diode (OLED) pixels [15].

In this work, we report the transfer of aluminum, polymers and bilayer building blocks for OLED. We studied the influence of the major parameters, such a laser fluence, transfer material and release layer thickness and unravelled the effect of the

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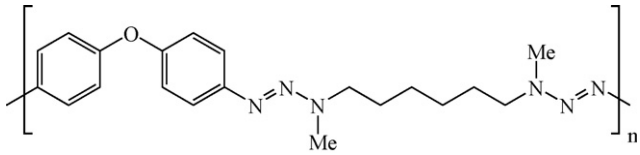

Fig. 1. Formula of the triazene polymer.

mechanical properties of the transfer material on the quality of transfer.

2. Experimental part

The multilayer donor films were prepared by coating successively fused silica substrates with the triazene polymer and the materials to transfer. The structure of the triazene polymer is shown in Fig. 1 and was synthesized as described in [16]. Films of triazene were prepared by spin coating from solutions in chlorobenzene and cyclohexanone (1:1, w/w). Aluminum was deposited by thermal evaporation in high vacuum. Gelatine (food gelatine, DGF Stoess, Germany) was spin-coated from an aqueous solution which had been stained with some drops of eosine dye. Methylcellulose (Methocel MC, Fluka, low viscosity) was spin-coated from an aqueous solution as well. The receiver substrates were glass plates, cleaned beforehand.

The transfer was achieved using a single pulse from a XeCl excimer laser (Compex, Lambda Physik, $\lambda = 308$ nm, $\tau = 30$ ns). The donor and the receiver substrates were placed in close contact (< 1 μm), perpendicular to the beam, on a motorized translation stage. The fluence was adjusted with an attenuator plate. A square mask with an aperture of 2 mm was applied to utilise a homogeneous part of the beam, which was focused by a lens onto the backside of the donor film with a magnification of 0.25, yielding a spot size of 500 μm. The pulse energy at each fluence was measured by a pyroelectric energy meter (Molectron J4-09 or Gentec QE 50) placed at the end of the beam line and an average on 100 pulses was used. For measuring some energy ranges, the intensity of the beam was reduced by a beamsplitter. A CCD camera with a microscopic objective was used to follow the deposition.

The computer-controlled system allowed to create a matrix of points for each sample, where the pulse energy was varied. The profile of the transferred patterns was measured by profilometry (Ambios XP-1 profilometer). Images were taken by an optical microscope (Zeiss Axioplan) coupled with a digital camera (Leica DC500).

3. Results and discussion

3.1. Transfer of metal pixels

The transfer of metal patterns has both theoretical and practical interests. As an evaporated layer, it can be deposited on triazene with a well-defined thickness and independently of the solvent used for the polymer. It can thus build a reference system for studying the influence of chemical modifications of triazene, e.g. side chain variation. Its mechanical properties are also well known and a force balance involving shear stress and pressure may be easily available. There is also a technological interest to direct-write metal patterns, for instance as electrical contacts on microelectronic devices. For the experiments, a constant layer thickness of 80 nm of aluminum was chosen. The influence of the laser fluence on the transfer is discussed at first. An overview of the donor (up) and receiver substrates (down) after the transfer is presented on Fig. 2 for various fluences. The triazene layer was 350 nm thick and each fluence was investigated twice. A clean transfer is achieved between 490 and 570 mJ/cm^2. The donor spot is delaminated, i.e. all the material is removed from the irradiated spot, and the material is transferred, i.e. the pixel can be found integrally on the receiver. No transfer and delamination occur at lower fluences, although the square edges are clearly cut-out, even at 200 mJ/cm^2. This

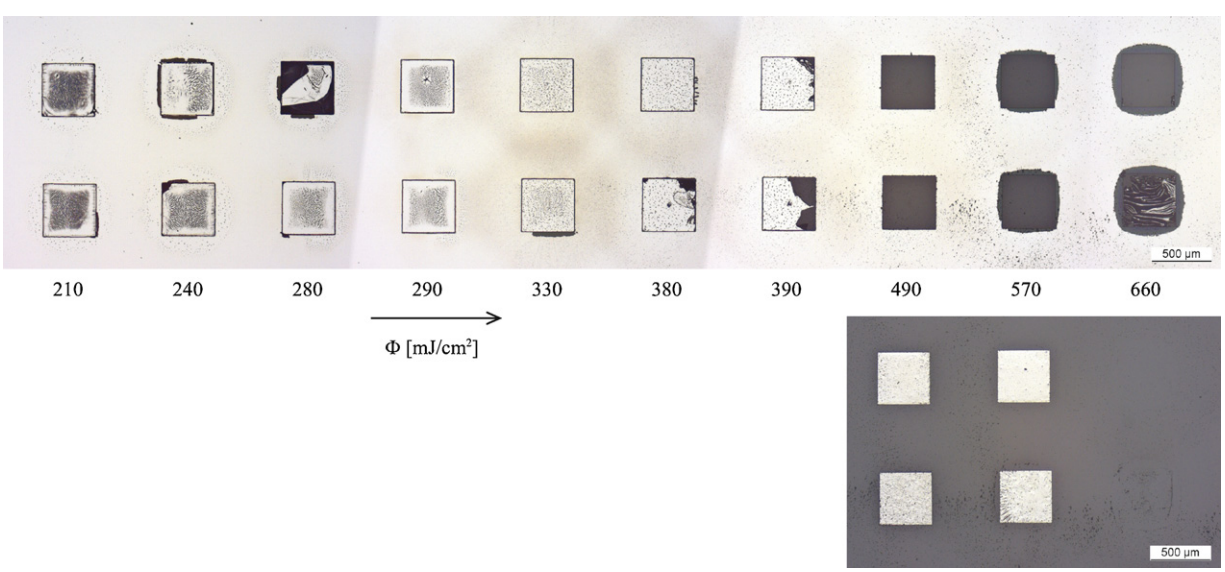

Fig. 2. Image of a donor (top) and receiver substrate (bottom) after transfer of aluminum. The receiver is shown only for the three highest fluences, as no transfer was observed in the other cases. The donor film was made of 350 nm triazene and 80 nm Al. Fluence (indicated) was varied horizontally and repeated twice (vertically).

effect is certainly helpful to avoid a tear-off of the Al film. Above 300 mJ/cm^2, a halo of black particles surrounds each spot. This might be the result of the triazene decomposition and shockwave propagation in the substrate plane, or more probably, direct ablation of the metal layer. Above 660 mJ/cm^2, only delamination occurs but no material is transferred.

There is an optimal fluence to find between an insufficient burst and an excessive irradiation of the transfer layer. At a too low fluence, not enough triazene is decomposed and the generated pressure cannot overcome the mechanical resistance of the overlaying material. On the opposite, when a too high fluence is applied, the triazene layer no longer acts as a protecting barrier and the transfer material receives a large amount of energy, causing damages by melting or direct ablation in the case of metal. The top layer is then fragilized and destroyed upon transfer.

Fig. 3(a) shows a magnified view and a profile of the transferred pixel at 570 mJ/cm^2, upper line. It has sharply defined edges and no holes. Some black particles are visible on and around the pixel, as mentioned above. The profile is quite smooth except for some spikes coming from these debris.

3.2. Influence of the transfer material

Our LIFT method is not only intended to transfer metal layers, but many other materials, in particular polymers. These have to be spin coated on the triazene to prepare the donor substrates. Therefore, they must be soluble in a different solvent than chlorobenzene or cyclohexanone, otherwise the release layer would be washed out during the spin-coating. To avoid this, two water-soluble polymers were chosen: gelatine and methylcellulose. Besides having different mechanical properties than metals, they are also possible carrier materials for the transfer of biological molecules or even cells.

The thicknesses of the triazene and top layers are given in Table 1, along with typical elastic moduli, tensile strengths and elongations of the top layer materials, taken from literature. Similar thicknesses were used for both samples, in order to allow direct comparison. Fig. 3(b) shows a transferred pixel of eosine-dyed gelatine with its corresponding profile obtained at 140 mJ/cm^2. The eges are sharp and the pixel is full. However, the surface is very rough. Gelatine is a protein and may have undergone denaturation and conformational change during the transfer, which leads to a possible spatial rearrangement and roughening of the surface. Another explanation is that the residual water trapped in the polymer network was brought to boil and produced bubbles within the layer. In both cases, this material is a very good indicator of the thermal stress induced by the process. A non-reproducible, partial pixel of gelatine (not shown) was obtained at a lower fluence (45 mJ/cm^2) and the microscopy as well as the surface profilometry revealed a very smooth surface in this case. Unfortunately the required fluence to get a full transfer is higher than what the transfer material can support without damages.

A transferred methylcellulose pixel is shown on Fig. 3(c) with its profilometry trace. The donor film had approximately the same thickness as for gelatine, but the fluence needed to achieve a good transfer was much higher, namely 620 mJ/cm^2. Clearly, the shape of the pixel is not so well delimited. The edges consist of teared out film that did not adhere to the receiver substrate. The profile of the donor substrate (not shown) indicates that the square of delaminated methylcellulose was larger than the laser spot size, defined by the triazene ablation crater. As seen from Table 1, the methylcellulose film is less stiff than gelatine but much more ductile. Instead of breaking into pieces, the pixel edges get folded upon transfer,

Table 1
Layer thickness and mechanical properties of the materials

	Aluminum	Gelatine	Methylcellulose
Thicknesses [nm]			
Triazene	350	100	90
Donor top layer	82	110	100
Transferred pixel	76	97	48
Elastic modulus [GPa]	28–71[a]	3.0–5.6[b]	1.2[c]
Tensile strength [MPa]	151–166[a]	77–115[b]	10–12[c]
Elongation to break [%]	18–23[a]	3.0–4.7[b]	7–14[c]

[a] From [18,19].
[b] From [20–23].
[c] From [24,25].

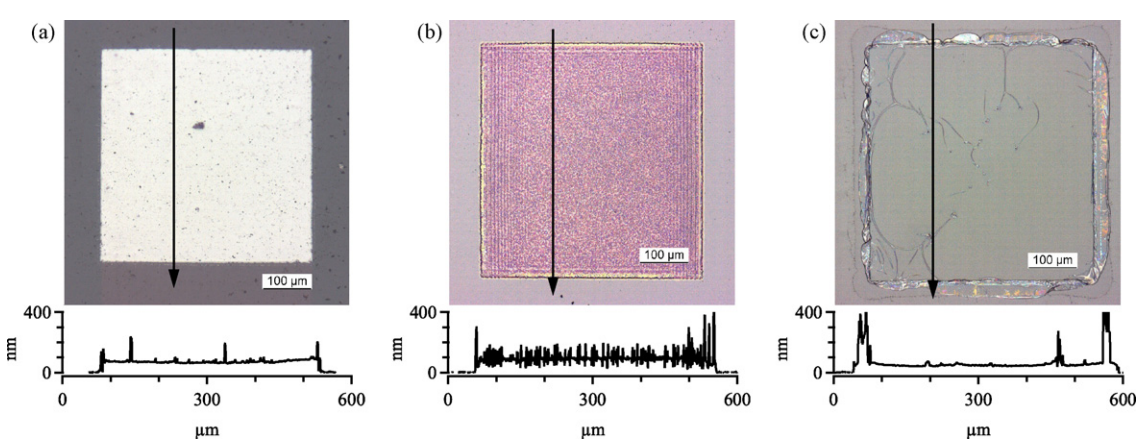

Fig. 3. Pictures and corresponding profiles of transferred pixels: (a) aluminum at 570 mJ/cm^2, (b) gelatine dyed with eosin at 140 mJ/cm^2, (c) methylcellulose at 620 mJ/cm^2. The location of the profile is indicated by the arrow.

which yields the ripples observed on Fig. 3(c). Except this, the film is very smooth and also visually free of defects.

An issue related to the large difference in fluence is the thickness of the transferred films. These values are summarized in Table 1 as well. While the transferred film of gelatine is almost as thick as the donor layer, the pixel of methylcellulose lost half of its thickness upon transfer. Obviously, a part of the methylcellulose layer was directly ablated by the high fluence pulse. A way to improve the transfer would be to use a thicker triazene layer, which would provide stronger propulsion while keeping a sufficient barrier to irradiation.

From these first experiments, it appears that a certain stiffness is required to get a sharp cut of the pixel. If the material is too soft, like methylcellulose, it will absorb the energy and deform. Aluminum and gelatine films allow sharp pixel transfer while the transfer of soft methylcellulose results in ill-defined pixels. As infered from the mechanical properties given in Table 1, the elastic modulus of methylcellulose is significantly smaller than the one of aluminum or gelatine. Consequently, the burst induced by the laser pulse will be largely dissipated in the soft methylcellulose film by deformation. Only a strong burst can induce the transfer, with the consequence of irradiating the top material. On the opposite, stiff materials like metals allow an easy delamination but have the tendency to break into pieces. Although the mechanical properties of films under fast strain rate (impact) may be very different from the static properties of the bulk, available in the literature, there is a hint that stiffness is an important parameter for controlling the transfer process. In correlation with the elastic moduli, high tensile strengths will result in sharp pixel transfer, while elongation to break does not seem to be critical in the present work. A deeper study of the influence of the mechanical properties on the pixel transfer would certainly help to get a clear picture of the mechanism.

3.3. Influence of the triazene thickness

The thickness of the triazene is important, because together with the applied fluence, it determines the amount of gas formed and the remaining thickness of non-ablated triazene. To assess these effects, transfer of aluminum was investigated with different triazene thickness (from 0 to 350 nm) while keeping the Al layer unchanged.

A clean transfer was only achieved with a thick layer of triazene (350 nm), whereas all thinner films did not yield satisfactory results. The primary hypothesis was that part of the triazene layer would stay on the metal film and mechanically stabilize it, and thus help the transfer. If this were the case, the transferred pixel would be thicker than the donor Al layer. From Table 1 we see that this is not true, the pattern on the receiver is slightly thinner than the starting film. Transfer of Al without release layer did not give good results under the investigated conditions. Only dark particles were deposited on the receiver.

More information can be gained from these experiments. For each sample, the fluence at which a complete delamination of the irradiated spot occurs was determined by visual inspection of the donor substrates. These delamination fluences are reported in Fig. 4. They depend strongly on the release layer thickness. For layers above 100 nm, the fluence increases with film thickness. A minimum is reached around 100 nm. Below that point, the fluence increases again with decreasing film thicknesses, up to the value measured without triazene layer. A comparison with the delamination fluence of pure triazene would certainly yield a good correlation and will be further investigated.

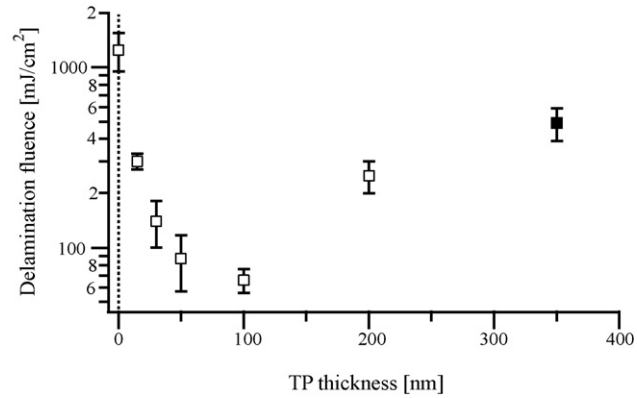

Fig. 4. Minimal fluence required for the delamination of Al donor pixels as a function of triazene thickness. The successful transfer condition is indicated by the filled symbol.

The trend between 100 and 350 nm is easily understandable, because a thicker film needs a larger fluence to be fully ablated. The values between 50 and 15 nm are also in accordance with the ablation behavior of very thin triazene films. We showed previously that due to thermal diffusion into the substrate and reduced absorbed energy, the ablation threshold of films below 50 nm was strongly increasing with decreasing thicknesses [17]. As the delamination fluence depends on the ablation threshold, the former will increase as well. Due to this, a thin triazene film cannot play its protecting role for the Al layer, and a large amount of energy impinges on the metal. Another effect may be important: tending to thinner layers, the amount of triazene becomes too small to provide the thrust needed for overwhelming the mechanical resistance of the metal. Therefore, delamination occurs by a mixture of triazene decomposition and metal ablation, which turns completely into the latter for a pure Al donor. As Al has a higher threshold fluence than triazene, the delamination fluence increases.

The triazene thickness appears to be a crucial parameter for the process, because it determines the fluence needed for delamination, which is a necessary but not sufficient condition to get clean transfer. For minimizing damages to the transfer layer, it is desired to work at the lowest fluence possible, thus with a triazene layer of around 100 nm in this case. Thinner films are not advantageous because the ratio between fluence needed and fluence transmitted is completely defavorable and the benefit of using a sacrificial release layer is almost lost. The upper thickness range is clearly the interesting zone, and further investigations need to be done to understand why transfer of Al requires a thick release layer.

3.4. Transfer of a bilayer system

After transferring metal and polymer patterns, the next step is to look at the transfer of a bilayer pixel made of Al and polymer. The choice of the top polymeric layer was guided by the final goal of our LIFT method, which is to transfer pixels of electroluminescent polymers for fabricating organic light-emitting diodes (OLED). We reported the successful transfer of bilayer pixels of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and Al onto a transparent anode and subsequent characterization of the so-formed OLEDs [15]. In this case, a donor film of 100 nm triazene, 70 nm Al and 90 nm MEH-PPV was used and pixels were obtained with 250 mJ/cm^2. It demonstrates that the transfer of a bilayer pixel is possible without altering the properties of the transferred materials, which is the critical test to assess the relevance of the technique. Further investigations will be carried out to determine the influence of the second transfer layer on the dynamics of the process.

4. Conclusion

Patterned metal and polymer layers can be transferred with our technique. The transfer is strongly influenced by the process parameters and only a narrow operating window leads to successful transfer. It seems that the stiffness of the film plays an important role to optimize the process. There is a minimal thickness of triazene required to benefit fully of the advantages offered by the dynamic release layer. Although the transfer method is still at an early developement stage, thin optoelectronic devices have already been fabricated by this technique.

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