Improvement in semiconductor laser printing using a sacrificial protecting layer for organic thin-film transistors fabrication

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A B S T R A C T
Laser-induced forward transfer (LIFT) has been used to deposit pixels of an organic semiconductor, distyryl-quaterthiophenes (DS4T). The dynamics of the process have been investigated by shadowgraphic imaging for the nanosecond (ns) and picosecond (ps) regime on a time-scale from the laser irradiation to 1.5 μs. The morphology of the deposit has been studied for different conditions. Intermediate sacrificial layer of gold or triazene polymer has been used to trap the incident radiation. Its role is to protect the layer to be transferred from direct irradiation and to provide a mechanical impulse strong enough to eject the material.

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1. Introduction

The interest in organic thin-film transistors (OTFT) has been increasing considerably over the past few years, because they offer unique opportunities in low-cost microelectronics. Laser-based processes offer versatile alternatives for the deposition of thin films in organic devices operating on flexible supports where the usual techniques cannot be used due to a lack of solubility, or in the case of complex device architectures fabrication.

The LIFT [1] process consists of transfer of a piece of a thin film previously deposited on a transparent donor substrate onto an acceptor substrate usually using a single laser pulse. This simple, single step, direct printing technique offers the ability to make localized deposition of material. It has been successfully applied for a wide range of material such as metals [2], nanotubes [3], powder [4], liquids [5], organics [6] and biomaterials [7].

The patterned deposition of thin organic semiconductor films is essential for the development of organic electronic devices. The p-type oligomer DS4T is a remarkably efficient semiconductor in the OTFT configuration but it does not possess the required solubility properties. It is a non-commercial semiconductor synthesized and purified by sublimation by the CINaM laboratory [8]. In this paper, we study the laser printing of this oligomer using the LIFT technique and discuss the dynamics of the transfer.

2. Experimental setup

In order to understand the mechanisms of the ejection and to determine optimal conditions of transfer, time-resolved visualizations have been carried out. This technique has already been achieved to study ejection and transfer of various materials [9–12].

Two different pulsed lasers have been used:

- Krypton fluoride (KrF) (EMG203MSC Lambda Physik) 35 ns @ 248 nm, 1–100 Hz, 0.5 J.
- Neodyme doped yttrium aluminium garnet (Nd:YAG) (Leopard S10/20 Continuum) operating on its third harmonic: 50 ps @ 355 nm, 10 Hz, 0.04 J.

Pulse duration has an influence on the heat diffusion, less thermal losses can be expected using the ps laser. The other motivation is to study the effect of the laser beam of a flat (ns laser) and a Gaussian (ps laser) energy profile on the flyer ejection and shape. The LIFT experimental setup has already been described elsewhere [13].
Shadowographic experiments were performed under atmospheric conditions using a continuous wave Nd:YAG laser (532 nm) as the light source to visualize the ejected material. Images were recorded with an ultra-fast intensified charge coupled device (CCD) camera every 100 ns from the beginning of the laser irradiation to 1.5 μs afterwards, with a gate width of 20 ns.

DS4T layers of 150 nm thickness were prepared by thermal evaporation under high vacuum (2 × 10⁻⁶ mbar at room temperature) on UV-transparent quartz suprasil. From analysis of the DS4T which is partially transparent to UV, we can calculate that for a 150 nm thick layer, 50% of the radiation is absorbed at 355 nm and 65% at 248 nm. A significant amount of energy is therefore transmitted through the layer and can easily damage the intended receiver substrate. Previous studies have shown that it is preferable to use a wavelength that is absorbed in the first few nanometers of the layer in order to minimize the area where thermal and photochemical effects take place [13]. The dynamic release layer (DRL) [14] technique is widely used for the laser printing of a large range of materials, especially sensitive materials such as biomaterials (DNA [15]) and devices such as OLEDs [16]. We report the study of the effect gold DRL. It has been chosen for its high absorption coefficient for both wavelengths (absorption depth = 13 nm @ 248 nm and 15 nm @ 355 nm) [17] and the layers were prepared by thermal evaporation under high vacuum. The receiver substrates were silicon covered by silicon dioxide (Si/SiO₂) (Vegatec). Morphology and thickness of the different deposited structures were investigated using optical microscopy (Zeiss Axioscope) and scanning electronic microscopy (JeolJSM20F) equipped with an energy dispersive X-ray analysis (EDX) system.

3. Result and discussion

3.1. LIFT printing without DRL

The LIFT printing of DS4T samples using ns and ps laser pulses was studied in order to determine the optimal conditions of irradiation. The donor and acceptor substrates were in close contact. The influence of the laser fluence on the transfer is discussed at first.

Images of printed pixels are presented in Fig. 1. The threshold energy fluence for transfer of a 150 nm thick DS4T film was found to be 0.10 J/cm² in ns and ps regimes (illustrated in Fig. 1Aa and Fig. 1Ba, respectively). In both case partial transfer was obtained and the printed pixel was not homogeneous, and some residual material remain in ablated region of the donor. A square shape of the deposited material was obtained by increasing the fluence (0.40 J/cm² in ns regime (Fig. 1Ab) and 0.20 J/cm² in ps regime (Fig. 1Bb) but splashes appear on both donor and acceptor substrates. They were outward ejected and covered an area twice of the deposit size. Part of the material was blown out of the irradiated zone under the action of thermo-mechanical effects induced during the laser/matter interaction indicating the destruction of a part of the layer. However the deposit of the ps regime was reproducible and its edges were well-defined.

Time-resolved shadowgraphic images of the ejected DS4T layer at various delay times after laser irradiation are shown for both laser pulse regimes in Fig. 2a and c. In both cases, these images clearly illustrate a shock wave propagating from the sample surface. The absorbed energy is dissipated in a thermo-mechanical way including formation and propagation of a shock wave, vaporization and ablation of the material. The ejected material, characterized by the dark area on the pictures, propagates perpendicularly from the sample surface with an acceptable flat propagation front. In the ns regime the average thickness of the flyer increases during its propagation, highlighting a loss of material cohesion. It is actually difficult to say if the observed flyer is still a solid layer of material or if it is a compact cloud of vaporized material. The flyer is visible at distances greater than half a millimeter and it is highly forward directed, the angular divergence is only 4. In the ps regime, the distance of material propagation is very limited, only 200 μm from the sample. The material was quickly destructed. After 1000 ns, only fragments are visible. Increasing the fluence leads to an increase...
of the initial velocity of ejection but the maximum propagation distance remains almost the same.

Fig. 3 presents a comparison of the traveling distance as a function of time delay. The physical description of the flyer trajectory is approximated to compare the data and to give an evaluation of the curvature of the trajectory [18]. One clear observation is that ejection following by a long distance propagation (>500 \mu m) of a DS4T material is only possible in ns regime, but for both laser regimes, the quality of the LIFT printed pixels was not good enough to proceed to OTFT development.

3.2. Influence of a metallic protecting layer

The same experiments of transfer and visualization were performed with 25 nm of gold DRL in both regimes. Our previous study with this DRL has shown that the best printing conditions are obtained when the film thickness is about twice the metal absorption depth, in this case 25 nm [13].
The threshold ablation fluence, corresponding to only a partial formation of the printed pixel was the same in ps regime 0.10 J/cm² (Fig. 1B,c) but it was noticeably increased in the ns regime: the threshold was found to be 0.30 J/cm² (Fig. 1A,c). However organic material was still remained in the donor irradiated area for these fluences. Fluences for which the quality of LIFT printed pixels was much improved, compared to a transfer without DRL, are 0.60 J/cm² in the ns regime (Fig. 1A,d) and 0.30 J/cm² in the ps regime (Fig. 1B,d), where the edges were more precisely defined and the quantity of ejected fragments and splashes has clearly decreased. At these higher fluences, debris of gold was appeared around and on the printed material, especially in the ns regime where the metallic DRL was destroyed over an area that is larger than the spot size. In both cases, such debris was very easy to remove with a modest airflow without altering the DS4T pixel adhesion.

In the ns regime, the ejection dynamics were very similar to the case where no DRL was used. The film ejection are shown in Fig. 2b. The thin film is ejected as a compact single piece with a flat front. However, analysis of the front velocity of the ejected material, especially in the ns regime where the metallic DRL was destroyed over an area that is larger than the spot size. In both cases, such debris was very easy to remove with a modest airflow without altering the DS4T pixel adhesion.

Material ejection was investigated with the ps laser as well. The thin gold DRL has improved the condition of the film ejection. It is interesting to note that the DRL allows to impart a higher kinetic energy to the organic layer. The flyers produced at a fluence of 0.20 J/cm² are illustrated in Fig. 2d. The laser absorption takes place in the gold layer, which was vaporized, and the semiconductor was ejected under mechanical stresses. The presence of the DRL probably has stabilized the flyer mechanically by forming a kind of composite film. The material cohesion was kept for a longer time. The angular divergence in this case was of order 10 while propagating over a distance of 1 mm.

The shorter pulse duration creates a much stronger shock wave and propels the flyer faster (Fig. 3), probably because the rate of pressure increase is much higher upon ps ablation, which can create a faster ejection of material. The velocities of the shockwave have been measured 25% faster than for ns ablation [19]. The second major difference between the two lasers is the shape of the flyer. The flyer ejected by ps irradiation has a curve and expanded shape compared to the nanosecond-generated flyer. The application of the Gaussian beam (ps beam) is not adequate for the transfer because the material ejection as well as the pattern transfer do not occur homogeneously. However, the pixels that have been transferred were obtained at much lower fluences than with the excimer laser and have revealed a smooth and crack-free surface. This suggests that a homogenized ps 355 nm laser beam may be a very promising way for LIFT and further investigations are carried out.

3.3. Deposits analysis

The transferred DS4T pixels without and with gold were investigated by SEM and are shown in Fig. 4 for ps regime. X-ray dispersive energy analysis (EDX) has revealed, on the deposit transferred with the gold DRL, the clear presence of residual metallic debris. The contamination was present in the micro and nanoparticles which cover the entire surface. The same condition is observed in ns regime. I(V) measurements have revealed conduction on the surface. Even if gold DRL has improved the ejection threshold and dynamics, the contamination on the printed pixel by itself is a huge drawback.

3.4. Optimization with an organic DRL

Previous studies reported successful printing of material with the use of a triazene polymer (TP) as DRL [9,16]. The TP has the particularity to decompose itself into volatile fragments at very low ablation thresholds upon ultra-violet laser irradiation. Layer
of 150 nm was prepared by spin-coating TP solution and annealing. Then the DS4T was evaporated on the TP film.

The best printed DS4T pixels in ps regime were obtained at 0.10 J/cm² (Fig. 5), corresponding to the half of the fluence used with gold DRL. All visual aspects of the deposit (surface homogeneity, sharpness of the edge, amount of ejected particles, presence of burned debris) were clearly improved. The absorption of the laser pulse has taken place in the TP layer, which was vaporized, and the semiconductor was ejected under mechanical stresses. Shadowgraphic images of the ejection are shown in Fig. 2e. The material was ejected in a compact shape, then expansion (lost of cohesion in the material) was occurred. The spatial position of the front part of ejected material as a function of time is shown in Fig. 3. The ejection dynamics with TP at 0.10 J/cm² and gold at 0.20 J/cm² were effectively similar.

4. Conclusion

In this paper we report LIFT experiments on organic semiconductor thin layers under different irradiation conditions and two different laser pulse durations. We have obtained a major improvement of the quality of the deposits for both regimes of pulse duration using a thin sacrificial gold DRL. The printed pixels are more homogeneous, the shape is better defined and the splashes outward ejected are reduced. The high directivity of the ejection and the distance of propagation show that DS4T structures with high spatial resolution can be performed using the LIFT-DRL technique. It has been shown that ps pulse allows the printing with lower fluences and propels faster flyer. However, gold is not adapted to act as DRL for semiconductor printing. The presence of debris on the entire deposit surface is a major problem for using these pixels in OTFT configuration. By this way, the first results with TP DRL are very promising to the printing of the sensitive DS4T semiconductor. Finally, a flat homogenized beam energy profile has been observed to be vital for the generation of stable and flat flyers.

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