Light-emitting polymer pixels deposited by laser-induced forward transfer

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Flatter screens and increasingly luminous and brilliant colour displays characterise the appearance of modern electronic devices. A next innovation step will be the development of flexible plastic displays which are no longer based on rigid carriers. Innovative laser-based microfabrication techniques in conjunction with organic semiconductor materials as well as functional polymers open up new possibilities for 'plastic electronics'.

Laptops, PDAs, multifunctional cell phones and miniaturized GPS receivers have recently become intimate companions in our daily life, and our digitally controlled world is now unimaginable without them. Integral to all these computerized gadgets is the digital display, as the user interface. Only enormous progress in flat screen technology has enabled it to reach its present state with respect to the size and design of such electronic accessories. The breakthrough for the fabrication of displays with small installation depths happened 30 years ago when liquid crystal display (LCD) modules first appeared on the market, initially masquerading as monochromic one-line number displays in pocket calculators and digital watches.

Liquid crystals as 'light valves'

The LCD technology is based on back-lighted display segments with a thin layer containing liquid crystals which can change transparency through the application of a trigger voltage. In this way the display segments can each be switched between clear brightness and darkness. Whilst single numerals can be displayed by the classic seven-segment symbols, the representation of an arbitrary graphic image needs a high-resolution matrix of tiny, regularly arranged, display segments which can be controlled as individual pixels for a graphical display. For a full-colour representation of a standard computer monitor, colours are generated by additive colour mixing of the three primary colours red, green and blue (RGB colour model). By

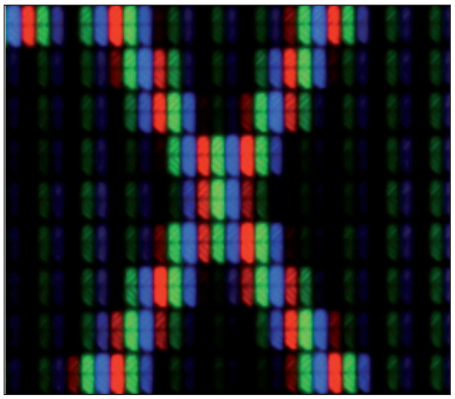

Figure 1: Magnified pixel structure of an LCD full-colour display. Every three adjacent sub-pixels – red, green and blue – form a square pixel with a size of typically 0.3 to 0.2 mm.

adjusting the luminosity of each primary colour's light component the full colour spectrum can be produced. Therefore, in a full-colour LCD screen, each single pixel unit consists of three small sub-pixels with colour filters for each of the primary colours (see figure 1). The graphic software communicates with each single sub-pixel and controls its individual transparency so that the two-dimensional grid of pixels on the screen produces a mixed colour image for the eye. Today, standard LCD computer monitors have a resolution of around 1200 pixels/cm^2 which are each composed of three separate RGB sub-pixels.

The liquid crystal segments do not themselves provide the light; homogeneous back-lighting is necessary (mostly cold cathode fluorescent lamps until now). The high energy consumption and the additional thickness to accommodate the back-lighting are two of the disadvantages of the LCD technology; others include the viewing angle-dependent contrast and the comparably slow response time of the liquid crystal which can make video images appear blurred.

Jacket sleeve displays

Displays made using novel organic light-emitting diodes (OLEDs) that emit light when triggered by a voltage could soon be an affordable alternative to LCD monitors. The most important advantages of such electroluminescent materials are that, from layers thinner than 1µm, high light-emitting efficiency and bright shining colours can be obtained, combined with significantly lower energy consumption. Each individual wafer-thin pixel emits its own light, meaning that no additional back-lighting is required. Additionally, the image produced has a much larger viewing angle than with current LCD technology. Displays only a few millimeters thick can be built which exhibit switching speeds high enough for video performance. Thanks to flexible material properties, the production of bendable or rollable ultra-thin organic-based displays is almost within reach. These display properties may permit, for example, integration directly into clothes, for uses such as a GPS display on the jacket sleeve, and will surely inspire thinner designs of future mobile devices.

Self-illuminating OLED pixels

In certain semiconducting materials electricity can be efficiently converted into light by charge-carrier (electrons and electron-holes) recombination. The light emission of every inorganic silicon-semiconductor LED is based on this recombination process. However, the production procedure for inorganic LEDs is a very complicated and demanding process due to the brittleness of the materials involved (e.g. Si single crystals). On the other hand, there are OLED displays, based on the same physical mechanisms, but involving innovative organic light-emitting compounds.

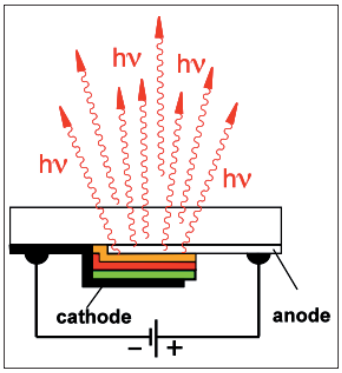

Figure 2: Schematic diagram of an organic light emitting diode (OLED). Sandwiched between the transparent anode (usually indium tin oxide) and a metal cathode are the thin layers of organic semiconductor materials and an electroluminescent compound which is lights up when a voltage is applied.

Though not as advanced in development as their inorganic counterparts, OLED optoelectronic devices are now being produced. Compared to inorganic LEDs, the construction principle of OLEDs is relatively simple, as shown in figure 2.

As a transparent anode compound, indium tin oxide (ITO) has been established as a good transparent conductor material, despite its high cost. In the manufacturing process of OLED devices, ITO is deposited as a thin anode layer on top of a glass carrier or a plastic film. On top of this, ultra-thin layers (some with a thickness less than 100 nm) of either organic semiconducting materials or light-emitting polymers, are deposited.

Simpler production

In terms of production costs, crucial advantages of OLEDs are expected to be achieved not only by lower material costs (the synthesis of organic semiconductors with tailored properties, compared to the growth of inorganic single-crystals), but also through cost-saving in the manufacturing process of the simpler multilayer stack architecture, nomatter whether the organic electroluminescent compounds consists of small molecules or polymers.

The fabrication of multilayer architectures, for thin-film electronic devices, requires the sequential and patterned deposition of thin layers. High-vacuum evaporation deposition techniques can be used for both organic molecules and inorganic compounds, but these are technologically demanding, slow and therefore expensive. However, solvent-based deposition techniques are also available for organic compounds. The use of soluble organic compounds opens up further processing possibilities, such as conventional printing methods, with a multitude of advantages. So far, solution-based printing methods such as ink-jet, screen printing and photolithography have been used; but such wet layer-by-layer deposition processes are often impeded by solvent compatibility issues.

An alternative novel micro-deposition technique based on laser-induced forward transfer (LIFT), which allows the precise direct write printing of light-emitting polymers as small solid pixels, is being developed in a joint research project between two Swiss federal research institutes, the Paul Scherrer Institut (PSI) and Empa, funded by the Swiss National Science Foundation.

The LIFT process for laser printing of organic materials

Laser Induced Forward Transfer has the potential for accurately depositing thin-films and printing successive layers of organic materials via a direct-write process. This technique uses a UV laser with a special UV-light absorbing polymer film which serves as a sacrificial release layer. The principle is schematically shown in figure 3, where a pulsed laser induces the forward transfer of a thin solid material layer from a transparent donor substrate onto a receiver substrate.

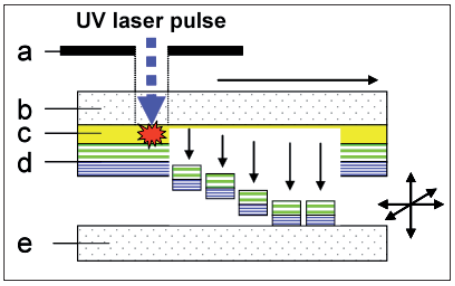

Figure 3: Principle of the modified laser-induced forward transfer (LIFT) process: (a) mask; (b) carrier substrate; (c) sacrificial thin film of "exploding" aryltriazene photopolymer serving as a pressure generator upon laser irradiation; (d) thin layers of transfer material; (e) receiver substrate with transferred pixels.

The release layer is a tailor-made polymer containing UV-decomposible aryltriazene chromophores (Ar–N=N–N<), covalently incorporated in the polymer main chain, which can be photochemically cleaved into nitrogen gas and small volatile organic fragments by UV-laser irradiation, as illustrated in figure 4.

Laser microcatapult for polymer pixels

This UV-absorbing release layer ('c' in figure 3) decomposes instantly upon irradiation with a short, well-focused UV laser pulse, and the evolving "ablation" products generate a laser-triggered pressure jet, which then punches out and catapults the overlying transfer materials integrally towards the receiver substrate. The spatial shape of the focused laser spot directly defines the outline of the catapulted pixel. Since the sacrificial polymer release layer protects the transfer layer from the incident UV irradiation, even highly sensitive materials can be gently transferred and deposited, materials such as semiconducting polymers or biomaterials. Compared with previous light-to-heat conversion layers frequently used with IR lasers, the UV-light triggered photodecomposition process significantly reduces the heat-load to the transfer layer,

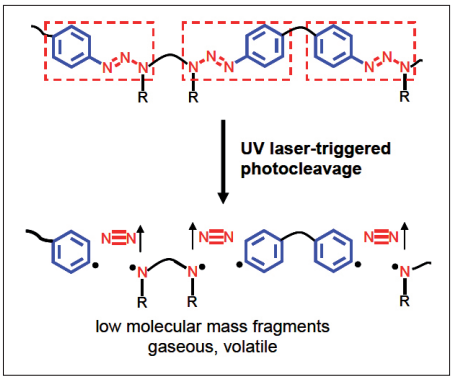

Figure 4: Schematic general structure of the UV-light absorbing polymers. The polymer contains triazene chromophore units (framed in red), which decompose upon UV-light irradiation into small volatile organic fragments and nitrogen gas.

a feature that is important for preserving the properties or functionality of sensitive materials.

Laser choice for LIFT

The aryl-triazene polymers used as the catapulting layer, were tailored to have an absorption peak that fits the XeCl excimer laser wavelength at 308nm. In the present context, the flatter beam energy profile of the excimer laser is its principle advantage over Gaussian solid-state UV-lasers, as this results in a much cleaner transfer. Transfer using other lasers has been studied and has shown how differences in pulse duration and beam energy profile affected the quality of the transferred material. Despite improving the catapulting efficiency, there was no clear advantage to using pulses shorter than the standard 30 ns pulse duration of the XeCl laser.

Micro-imaging of the transfer process

Figure 5 shows the pump-probe imaging technique known as shadowgraphy that was used to gain insight into the dynamics of the LIFT process.

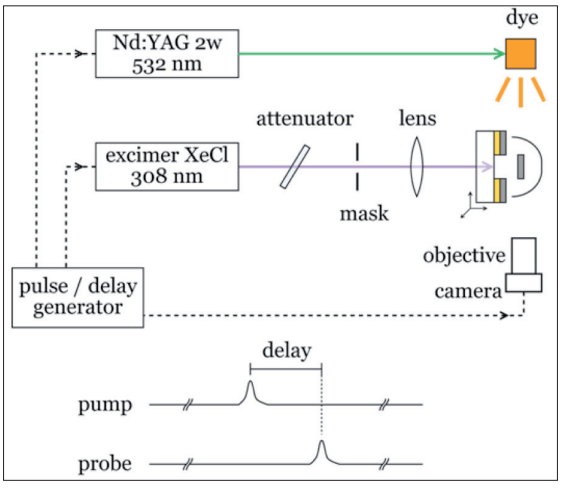

Figure 5: Setup for two laser "pump-probe" shadowgraphy for time-resolved imaging of the forward transfer processes.

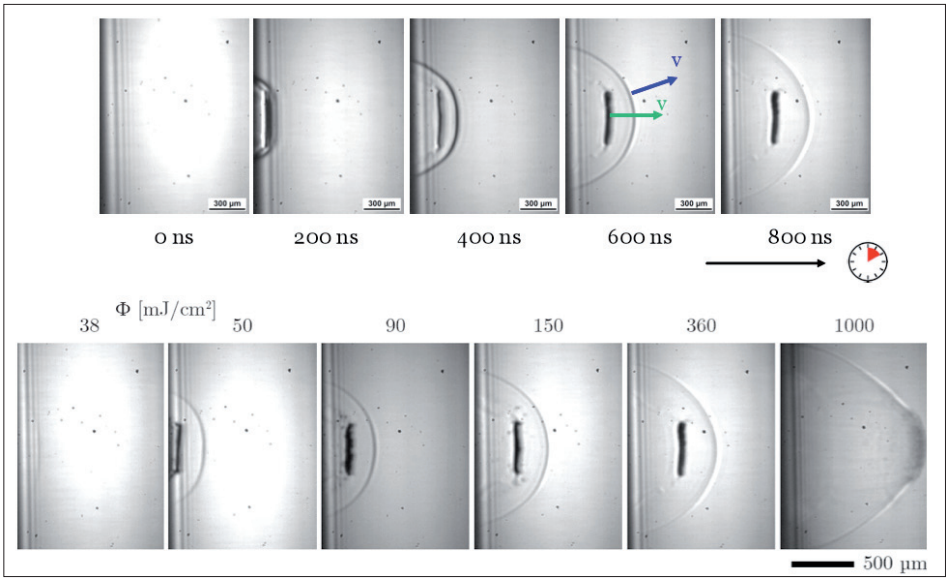

Figure 6: Shadowgraphy micro-images of the time-resolved development of the shockwave and flyer ejection for a laser fluence of 360 mJ/cm² (upper row). The flyer consists of a layer of 80 nm aluminum which was coated on top of a 350 nm thick triazene photopolymer. The flyer stays stable over a distance of more than 0.3 mm. The image sequence shows the different propagation speeds v of the flyer and the shockwave. Second row: The forward-ejection of the same model system was studied to investigate the fluence dependence of the generated thrust. Images are taken each at a constant delay time of 800 ns after the laser pulse. Flyer velocity and shockwave shape depend on the applied laser fluence.

Shock waves are generated by the laser-triggered "micro-explosion" of the catapulting layer, and their strengths depends on the pressure of the ambient atmosphere. Figure 6 shows the ejection process of a model pixel flyer in an ambient atmosphere,revealing the evolving shockwave and the catapulted pixel. Note especially that the shape and morphology of the catapulted pixel stays intact over a distance of more than 300 µm. The bottom row of images shows the influence of laser pulse energy on the pixel flyer speed and shockwave shape, which allows a fine tuning of the transfer conditions at low fluences. At fluences exceeding 1 J/cm² the flyer accellerates into the shockwave and is destroyed.

Orange light miniature OLEDs

After a number of years' research and development work, the two Swiss research teams recently achieved a breakthrough, proving the validity of the modified LIFT technique by successfully fabricating their first miniaturized OLEDs. With single laser pulses, micropixel stacks of the electroluminescent polyparaphenylene vinylene derivative (MEH-PPV) and the aluminium cathode, were directly printed onto the ITO anode in one step, as shown in figure 7.

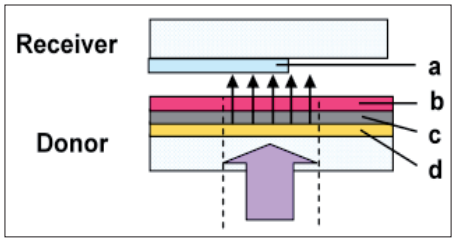

Figure 7: Layer architecture of the donor and receiver substrate for the pixel transfer: (a) Transparent indium-tin-oxide (ITO) anode; (b) thin layer (20 – 40 nm) of the electroluminescent polymer MEH-PPV; (c) aluminium cathode (70 nm); (d) aryltriazene photopolymer film (100 nm). The incident laser pulse decomposes the sacrificial photopolymer layer 'd' and catapults the bilayer system 'c/b' in one step towards the receiver surface.

The transferred pixel required only to make contact with a DC current for the emission of orange light (see figure 8). The functionality of operating devices was characterized by current-voltage and electroluminescence measurements which proved that the integrity of the transferred materials has been fully preserved during the improved LIFT deposition process. Using a mask to shape the laser beam a pattern of multiple pixels may be deposited with a single pulse, providing a promising method for the production of full-coloured displays on flexible substrates.

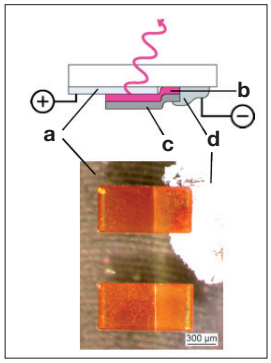

Figure 8: Resulting OLED pixel after transfer: the MEH-PPV layer (b) and cathode (c) are printed onto the ITO anode (a). The photograph shows two pixels seen through the ITO-coated substrate. After contacting with silver paste (d) the pixel shows an orange-red light emission.

Biological applications

Interest in this Swiss development has come from many other fields: recently, an international research collaboration has demonstrated that the modified LIFT process can transfer not just sensitive materials, but also living mammalian neuroblast cells. With the aid of a ~100nm thick aryltriazene photopolymer film the cells were deposited precisely onto a biological substrate, gentle enough that the functionality was not impaired, and the cells started reproducing instantly. This opens up new possibilities for the manufacture of biosensors in which living cells should be precisely deposited onto microchips.

Thus far, the applications for the photosensitive special polymers as the absorbing sacrificial release layer in the laser catapulting process are still in the early research and development stage. The emergence of flexible plastic monitors may still be a few years away but it is already clear that ultra-thin OLED and polymer displays will rival the current leaders in the digital display market.

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Links

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