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Unconventional, Laser Based OLED Material Direct Patterning and Transfer Method

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1. Introduction

Organic light emitting diode (OLED) displays have a number of desirable features such as high contrast and brightness, wide color range, thin structure and light weight, among others.(Hirano et al. 2007) OLED displays have several manufacturing requirements such as large area scalability and an increasing push towards smaller feature sizes, tighter feature shape control, high yield and low cost. However, traditional lithography and thermal evaporation deposition techniques have significant disadvantages, including the need for masks that are typically difficult to make to the required specifications at a reasonable price. The conventional vacuum deposition and photolithographic patterning methods are well developed for inorganic microelectronics. However, organic electronics materials are chemically incompatible with corrosive etchants, resists and developers used in conventional integrated circuit (IC) processing. In practice, conventional IC fabrication processes are subject to limitations, in that they are multi-step, involve high processing temperatures, toxic waste and are therefore expensive. Furthermore, the increasing size of electronic devices such as displays poses great difficulty in adapting standard microfabrication processes, including lithographic patterning. (Zschieschang et al. 2003, Ko et al. 2007)

Therefore, there is a strong need to develop a novel process instead of complex modification of conventional vacuum deposition and photolithography based processes. OLED display manufacturing employs direct write techniques for patterning the various materials. Examples of OLED material direct write technologies include ink jet printing (Hashimoto et al, 2006, Gohda et al. 2002, Lee et al. 2002,, Kobayshi et al. 2002, Shirasaki et al. 2004, Fleuster et al. 2004, Lee et al. 2005, Saafir et al. 2005) screen printing (Shinar et al. 2007, Lee et al. 2009) and laser induced forward transfer (LIFT) (Hirano et al. 2007, Piqué et al. 1999, Suh et al. 2003, Willis et al. 2005, Kyrkis et al. 2006). As described in a recent review on OLED RGB patterning, success of an OLED patterning scheme depends on the material type, device design, pixel array pattern, display format, substrate size, placement accuracy, process TACT-time, and defect density. The type of material and OLED architecture largely determine which type of RGB patterning can be applied. Other factors determining the

viability of the patterning method for active matrix organic light emitting diode (AMOLEDs) depend on the given material set. (Lamansky et al. 2005) Solution processible direct write technologies such as inkjet printing and screen printing are subject to a number of limitations such as the need for solvent removal and contamination into the deposited material. Additionally, the minimum feature size is heavily influenced by the properties of the fluid used to deliver the material of interest and multilayer structure fabrication is difficult. (Kyrkis et al. 2006) Vacuum-processable OLEDs have been patterned mostly by deposition through a shadow mask or fine-metal mask (FMM). (Kang et al. 2003) Deposition can be accomplished either as a conventional physical evaporation or organic vapour phase deposition (OVPD), but FMM-related patterning issues are largely independent of the deposition technique. Remaining FMM patterning issues include difficulty of fabricating high resolution masks for large-area displays, mask lifetime and cleaning, particle contamination, and thermal expansion effects.
In this chapter, unconventional OLED material direct patterning and transfer methods especially laser based forward transfer and patterning approaches will be presented as promising potential alternative to conventional OLED fabrication methods.

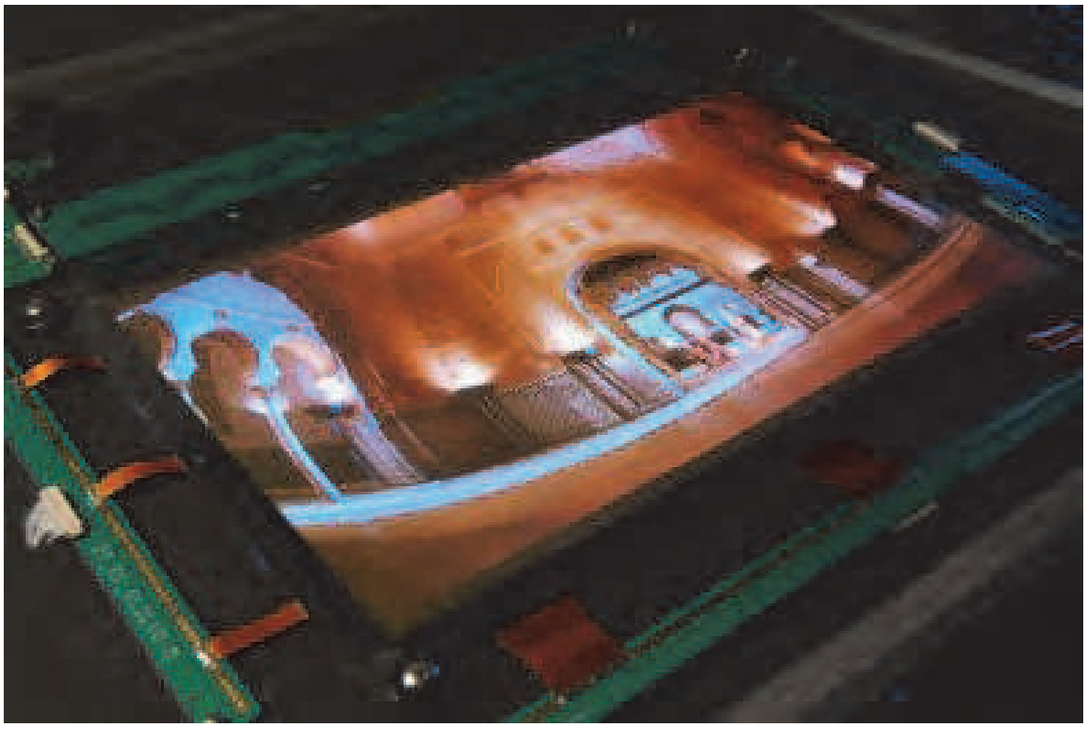


Fig. 1. 14 inch OLED display from CDT (Cambridge Display Technology) from CDT ltd.

2. OLED material laser induced forward transfer and patterning techniques

LIFT techniques pattern and transfer materials of interest by laser induced localized thermal evaporation or chemical decomposition of dynamic release layer. This dynamic release layer is the crucial part of the LIFT process and can be (a) a part of material of interest, (b) specially designed light absorbing thin intermediate layers in LITI (laser induced thermal imaging) (Lamansky et al. 2005, Blanchet et al. 2003a, Suh et al. 2003) and LIPS (laser

induced pattern-wise sublimation) process (Hirano et al. 2007) or (c) a mixture of active or sensitive material in a UV absorbent matrix in MAPLE DW(matrix assisted pulsed laser evaporation direct writing) (Piqué et al. 1999, Arnold et al. 2007) process. LIFT and several variations have demonstrated deposition of metals, metal oxide films, inorganic dielectric films, ceramics, and polymer and biomaterials. (Arnold et al. 2007, Willis et al. 2005, Kyrkis et al. 2006, Chrisey et al. 2003) Most notable recent advance in LIFT technique is the OLED pixel fabrication using dialkyltriazene polymer as an UV-absorbing and decomposing intermediate sacrificial layer compared with thermal decomposition. (Rardel et al. 2007)

However, most LIFT based techniques in OLED material transfer process still exhibit a number of limitations such as laser selection (wavelength, fluence), resolution, and edge sharpness. Most LIFT based techniques apply ultraviolet (UV) or infrared (IR) laser with relatively high laser fluences (1~10 J/cm^2) to obtain enough pressure for ablative material transfer. UV or IR lasers need complex and expensive laser and optic system. Furthermore, without strict design of light absorbing layer, high power UV or IR lasers have high possibility for organic material damage during the LIFT process because generally organic materials have strong UV and IR absorption bands attributed to electronic and vibrational transitions, respectively. Besides thermal degradation, high laser threshold laser can also induce mechanical cracks on transfer material and problem in edge sharpness. Also resolution was usually limited to 50 to 100 μm.

Ko et. al. reported a nanomaterial enabled laser transfer (NELT) to facilitate the high resolution patterning and transfer of the heat-sensitive OLED material with more versatile laser wavelength selection with one or two order smaller laser energy than conventional LIFT processes. This is characterized by the introduction of an efficient light absorbing, loosely connected nanomaterial layer and the choice of laser wavelength that although is strongly absorbed by the properly engineered nanomaterial, it interacts only weakly with the organic material of interest, leading to effective evaporation and transfer of the material with less damage potential.

2.1 Laser Induced Thermal Imaging [LITI]

Over the last twelve years, we at 3M have developed Laser Induced Thermal Imaging (LITI) as a high resolution, digital patterning technique with a large number of potential applications including the patterning of digital color proofs, plates, and film; LCD color filters, black matrix, and spacers; field emission display (FED) anodes, contrast enhancement filters, and nanoemitters; organic field effect transistor (OFET) fabrication; and OLED emitters, color filters, and color conversion filters. Since 2000, 3M has partnered with Samsung SDI to jointly develop the process for AMOLEDs. (Wolk et al, 2004)

LITI involves the use of a precoated donor film, a large format laser exposure system, and a receptor (e.g. an AMOLED backplane) (Fig. 2). For OLEDs, a stock roll of functional non-transferring layers is prepared and stored. Solvent coating or vapor deposition is used to deposit an ultrathin (e.g. 20-200 nm) layer of red, green, or blue emitting transfer layer(s) to the stock roll shortly before patterning. Patterning of each color is then accomplished by first aligning the receptor (e.g. an AMOLED backplane) to the laser exposure system and then laminating a donor film to the aligned receptor. After the alignment step, the laser system is used to expose the laminated assembly. Exposed regions are released from the donor and adhered to the receptor. The process is repeated from two or more times, depending upon the OLED construction. Alignment is performed only once. (Wolk et al, 2004)

Once a donor is used to pattern OLED materials, it is discarded. Although the transferred area represents less than a third of the coated surface, the exposed donor film now contains a high resolution pattern. Dimensional instability of the film and the physical changes that the film undergoes during the exposure process make it impractical to reuse the exposed donor. (Wolk et al, 2004)

3M's LITI Process is well suited for use in the manufacture of high precision flat panel displays, where high resolution, absolute placement accuracy, and large format imaging are all required. The advantages of the LITI process are significant in situations where the separation of coating and patterning steps resolves a fundamental process. LITI applications include patterning of organic electronic materials for OLEDs and organic transistors, patterning of multilayered OLED stacks, patterning of polarizers or nano-emitters, and the potential of patterning enzymes and other biomaterials. (Wolk et al, 2004)

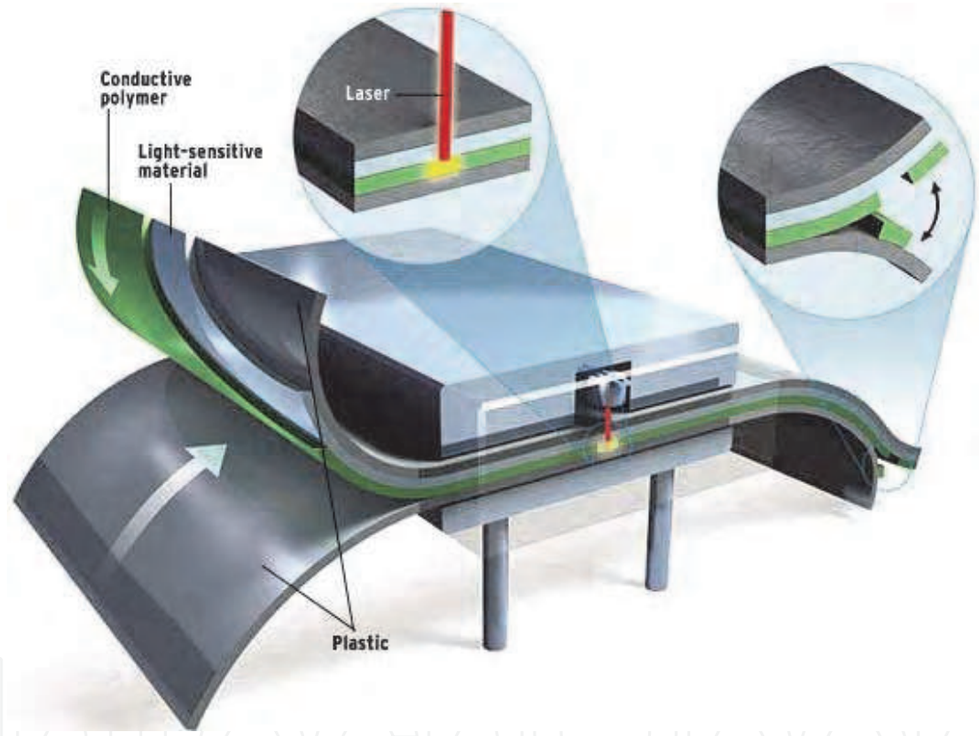


Fig. 2. LITI process schematics. (Blanchet et al. 2003b)

LITI is an emerging technology for high-resolution patterning of materials, including but not exclusive to both solution- and vacuum-processable OLED material sets. (Lamansky et al. 2005) Base steps in the LITI process include deposition of the material to be patterned (transfer material) onto a specially designed donor film, precise optical alignment of a large format laser imaging system to device substrate (receptor) fiducials, lamination of the donor onto the substrate, and patterning of the transfer material onto the substrate by selective exposure of the donor-transfer material-receptor stack to laser radiation. Conversion of laser radiation to heat is achieved in a light-to-heat conversion (LTHC) layer(s), which typically utilizes carbon black as a black body absorber. To generate a patterned RGB OLED display, optical alignment is performed only once, but lamination and exposure have to be performed for at least two colors.

Advantages of LITI over other patterning methods include its applicability to a broad spectrum of OLED material sets, high patterning accuracy (±2-5 μm compared to ±15-20 μm for shadowmasking and ink-jet techniques), ability to pattern multilayer structures in a single step, scalability of the process to large mother glass sizes, and ability to meet TACT time requirements. It is possible that LITI introduces thermal defects in the OLED materials during patterning, but by fine-tuning process conditions, donor structure, and OLED composition, occurrence of such defects can be minimized. The process is also sensitive to particulates and similar contamination of substrate (receptor in LITI terms) and donor surfaces. This puts stringent requirements on the donor, substrate and transfer atmosphere cleanliness.

2.2 Laser Induced Patternwise Sublimation [LIPS]

White OLED with color filter (WOLED+CF) methods and thermal transfer technologies are expected as alternatives to precision mask patterning. Sony demonstrated the WOLED+CF prototype display at SID 2003 (Kashiwabara et al. 2004). However, high power consumption and color impurity are the issues of this method for the TV application. Laser-induced thermal imaging (LITI) (Lee et al. 2004) and radiation-induced sublimation transfer (RIST) (Boroson et al. 2005) have been proposed as thermal transfer technologies. They have some concerns in production process. In the LITI process, contact between the donor film and the emitting area will degrade the device and transfer quality. Though RIST is a sublimation process without the contact, OLED material will be damaged by gases (e.g. O_2, H_2O etc.) released from a polyimide film donor during laser-heating. In addition, they require high precision technique to set flexible film on a large scale glass substrate uniformly without adhesive agents. Imprecise setting of a film donor lowers transfer performance. (Hirano et al 2007)

Sony has proposed a novel laser transfer technology for manufacturing OLED displays. Laser-induced pattern-wise sublimation (LIPS) has been developed to image RGB pixel pattern. OLED materials are precisely patterned from glass donors to a substrate by a scanning laser beam. The LIPS device performance is examined in comparison with conventional evaporated devices. Using this technology, a 27.3-inch active matrix (AM) OLED display has been fabricated. (Hirano et al 2007)

LIPS is a laser thermal transfer process. Two systems has been prepared, as shown in figure 3, in order to develop the LIPS process. One is the laser transfer system composed of alignment equipment, a step-moving (X-axis) laser head and a scanning substrate stage (Y-axis). The radiation source is an 800 nm diode laser. A width of the laser beam is adjusted in accordance with that of the transferred pattern. The other is the vacuum chamber where a glass donor is fixed on a substrate with clamping equipment. (Hirano et al 2007)

Figure 3 also shows the process flow diagrams of LIPS. A glass donor is necessary for each emission layer (EML) to be patterned. Organic material is deposited in a conventional evaporator on a glass donor covered with molybdenum absorption layer. Organic common layers such as a hole injection layer (HIL) and a hole transport layer (HTL) are formed on the glass substrate including a pixel defined layer (PDL) and bottom electrodes, as shown in figure 1(d). The substrate and the glass donor are introduced without exposure to the air and spaced apart in the vacuum chamber. And then the glass donor is put on the substrate and fixed by the clamping equipment. It is moved out of the chamber onto the stage of the laser transfer system in the atmosphere after introducing inert gas into the chamber. The

transfer gap between the glass donor and the substrate is precisely controlled all over the substrate by the rigid donor, the PDL and atmospheric pressure. Moreover the PDL prevents the donor from contacting the emitting area on the substrate. After mechanical alignment of the substrate to the laser head, laser beam scans and heats the designated position of the glass donor and organic material is transferred to the substrate by vacuum sublimation. The transferred organic material functions as an EML. The gap atmosphere is kept vacuum by the clamping equipment during the laser transfer. The patterning process is done for each emission layer. Common layers such as an electron transport layer (ETL) and a top electrode are formed on the patterned substrate after removing the donor glass in inert gas. (Hirano et al 2007)

From the viewpoint of productivity, the laser transfer process in the atmosphere can simplify a production system and improve laser positioning accuracy. Multiplying laser beams promise high throughput even for large-scale mother glass. Glass donors can be re-cycled, which saves the production cost. (Hirano et al 2007)

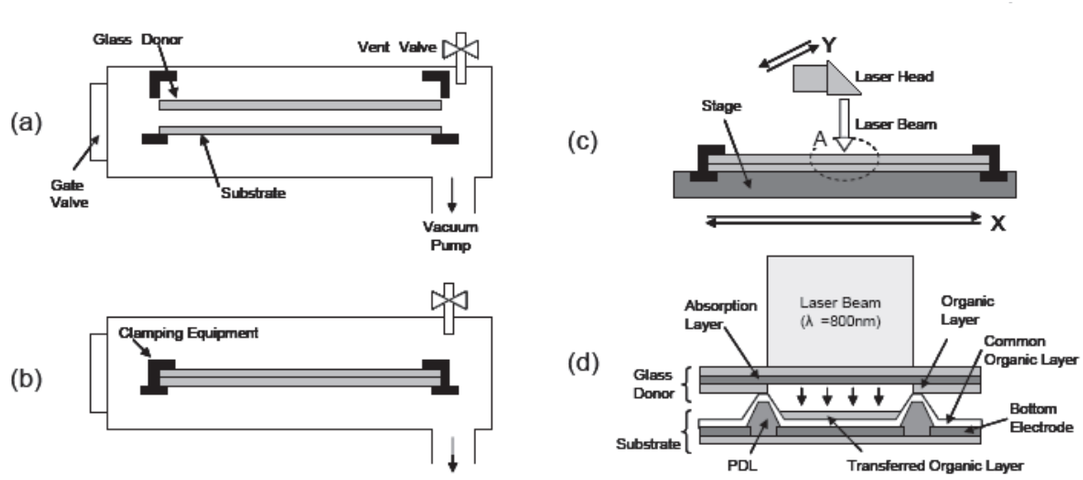


Fig. 3. Schematic diagrams of the LIPS process. (a) Placement of the glass donor and the substrate in the vacuum chamber (b) Setting of the glass donor on the substrate with clamping equipment (c) Placement of the substrate on the laser transfer system (d) An enlarged cross-section diagram of A in figure (c). (Hirano et al 2007)

The gap between a donor sheet and a substrate is critical to transfer accuracy. The advantage of the LIPS process is high precision by use of a glass donor instead of a film donor. The position accuracy is better than 4um. The pattern width variation is within ±2.0um. Using the patterning accuracy, we can realize high aperture ratio more than 60% for large-sized OLED display. The further improvement of patterning accuracy is possible by mechanical adjustment. (Hirano et al 2007)

2.3 Matrix Assisted Pulsed Laser Evaporation – Direct Writing [MAPLE-DW]

MAPLE DW was originally developed as a method to rapidly prototype mesoscopic passive electronic devices such as interconnects, resistors, and capacitors. (Piqué et al. 1999, Chrisey et al. 2000) This technology falls under the category of a "direct-write" approach because, in the same manner as a pen or pencil, it can be used to rapidly form any pattern with the aid

of CAD/CAM systems. The schematic of the apparatus is shown in figure 4. The material to be transferred is mixed in a laser-absorbent matrix and coated onto a support, or ribbon, that is transparent to the laser irradiation. A focused laser pulse is directed through the backside of the ribbon so that the laser energy first interacts with the matrix at the ribbon interface. The laser pulse is focused at the matrix-ribbon interface by a UV microscope objective that also serves as an optical guide to determine the area of the matrix to transfer. Layers of matrix near the support interface evaporate due to localized heating from electronic and vibrational excitation. This sublimation releases the remaining material further from the interface by gently and uniformly propelling it away from the quartz support to a substrate positioned 25 μm to several mm away. By removing the ribbon and allowing the laser pulse to interact with the substrate, this approach is also able to micromachine channels and through vias into polymer, semiconductor, and metal surfaces. All micromachining and material transfer can be controlled by computer (CAD/CAM), which enables this tool to rapidly fabricate complex structures without the aid of masks or moulds. When applied to polymers and composites, MAPLE-DW has produced 2-D and 3-D patterns as well as functioning devices. One such device was a chemoresistor fabricated by depositing a polymer/carbon composite (polyepichlorohydrin/graphite mixture) across two electrodes.(Piqué et al. 1999) This device retained function as demonstrated by sensitivity to chemical threats. In addition, polymer thick film (PTF) resistors were fabricated using epoxy-based materials.(Modi et al. 2001) The fabricated PTF resistors spanned four decades of sheet resistances (10 Ω/sq. to 100 k Ω/sq.) and performed consistent to theoretical models for temperature and frequency variance.

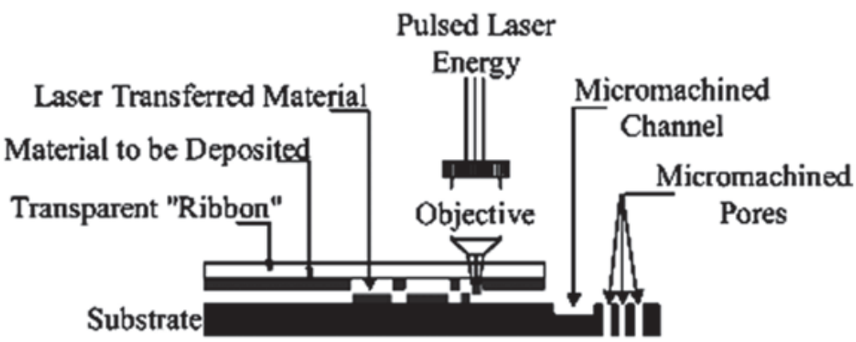


Fig. 4. Schematic diagrams of the MAPLE-DW deposition system. (Chrisey et al 2003)

2.4 Nanomaterial Enabled Laser Transfer [NELT]

Many of the direct write technologies mentioned above are subject to a number of limitations such as the need for solvent removal and contamination into the deposited material for ink jet printing. Additionally, the minimum feature size is heavily influenced by the properties of the fluid used to deliver the material of interest.

The conventional LIFT techniques also exhibit a number of limitations as they involve localized evaporation of either the material of interest or the light-to-heat converting intermediate layer resulting from the laser induced temperature rise. Laser-based techniques have been used successfully to deposit metals, metal oxide films, inorganic dielectric films, and ceramics,(Willis et al. 2005, Kyrkis et al. 2006, Chrisey et al. 2003, Arnold et al. 2007) but have limited success to the deposition of organic materials.

Generally, organic materials have strong ultraviolet (UV) and infrared (IR) absorption bands attributed to electronic and vibrational transitions, respectively as shown in figure 5. Therefore, UV or IR lasers have been typically used for organic material laser transfer by the direct laser absorption in the same organic material or a separate light absorbing organic material. However, organic compounds have high vapor pressures and can be easily damaged by thermal decomposition or degradation induced from photodecomposition by direct UV absorption or thermal decomposition by IR absorption. This is also the case even using an additional light absorbing organic layer. To overcome this problem, a thin metal film layer can be introduced as visible laser light absorber. However, this may cause organic material thermal degradation because the metal film usually has high melting or ablation threshold and exhibits inefficient energy coupling due to high reflectivity.

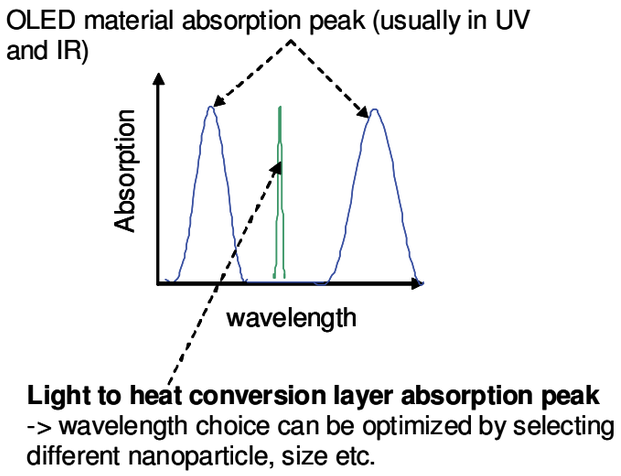


Fig. 5. Light to heat conversion layer engineering for OLED laser transfer

Ko et al. reported a nanomaterial enabled laser transfer (NELT) method to facilitate the patterning and transfer of the heat-sensitive OLED material. This is characterized by the introduction of an efficient light absorbing nanomaterial layer and the choice of laser wavelength that although is strongly absorbed by the properly engineered nanomaterial, it interacts only weakly with the organic material of interest, leading to effective evaporation and transfer of the material with less damage potential. (Ko et al. 2008)
The illustration of the NELT process and the donor multilayer is shown in Figure 6(a). Either a large area homogenized beam or a tightly focused Gaussian Nd:YAG pulsed laser beam (wavelength = 532 nm, pulse width = 5 ns FWHM) were applied normal to the donor substrate to induce the local heating of nanoparticle and the transfer of a target film onto a receptor substrate. The homogenized Nd:YAG laser beam cross section was shaped to a 0.9 × 0.9 mm2 flat top beam profile of good spatial uniformity by a micro-lens laser beam homogenizer while the tightly focused laser beam size had a 2~10 μm (FWHM) $1/e^2$ diameter Gaussian profile. The applied laser fluence was around 0.05~0.15 J/cm^2. The donor was composed of three parts; transparent substrate (glass slide) / laser-to-heat conversion layer (nanomaterials) / target material (OLED material). Self assembled monolayer (SAM) protected silver nanoparticles (Ag NPs) (30~40 nm sized, Figure 6(a) insets) were used as the laser-to-heat conversion nanomaterial layer by spin-coating on the glass substrate to form a 100~200 nm layer. The SAM coating serves to stabilize the Ag NPs and prevent

coalescence into a bulk film. (Korge et al. 1998) The optical property measurement by spectroscopic ellipsometry (Figure 6(b)) shows the NP film has strong absorption around 530 nm facilitating highly efficient energy absorption to the NPs laser while the polymer material exhibits little absorption. The target OLED material was tris-(8-hydroxyquinoline)Al (Alq3) layer deposited by a resonant infrared pulsed laser deposition (RIR-PLD) technique to form 200~300 nm layer on top of Ag NP film on a glass slide. The donor substrate was then placed in intimate contact with the receptor substrate in ambient air environment. The receptor substrate was a glass substrate with thin PDMS layer on top as an adhesion promoter.

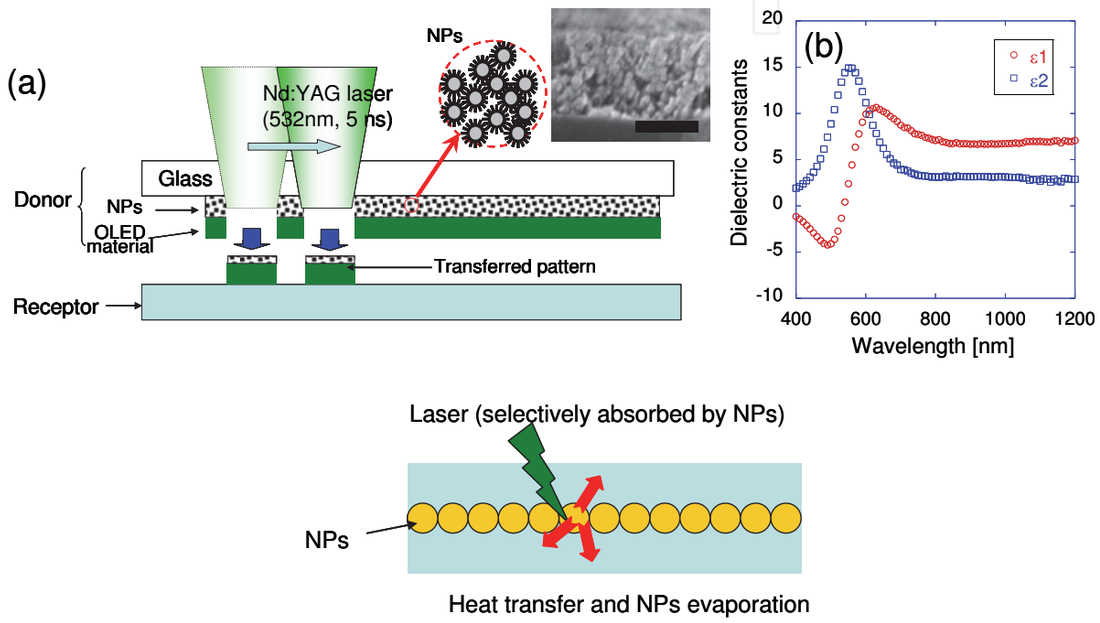


Fig. 6. (a) Schematic illustration of the NELT process and the donor multilayer (Alq3/Ag NPs/glass) structure. The inset pictures are schematics of SAM protected NPs and the SEM picture of the spin coated Ag NPs. Inset scale corresponds 100nm. (b) Ellipsometric measurement of the NPs film optical property. (Ko et al. 2008)

Figure 7(a-c) shows fluorescence pictures of (a) a donor substrate and (b,c) transferred Alq3 patterns on a PDMS/glass substrate after homogenized Nd:YAG laser transfer. The black squares in Figure 7(a) mark donor regions where single laser pulses (0.07 J/cm^2) transferred corresponding Alq3 patterns (0.9×0.9 mm^2 squares with 2 mm pitch) on a receptor substrate (Figure 7(b)). Figure 7(d) shows the donor cross section SEM picture near the laser beam edge and figure 7(e,f) show the corresponding magnified pictures. The micrograph of individual transferred Alq3 pattern (Figure 7(c)) and the SEM picture (Figure 7(g)) indicate that the transfer was very successful with well-defined edges and strong fluorescence without any visible cracks on the Alq3 surface. If the Alq3 layer becomes damaged, the layer will cease to fluoresce or the intensity will be greatly reduced. The thickness of the transferred layer was about 200 ~ 300 nm corresponding to the thickness of the Alq3 layer on the donor substrate structure as well as a small amount of the nanoparticle matrix layer.

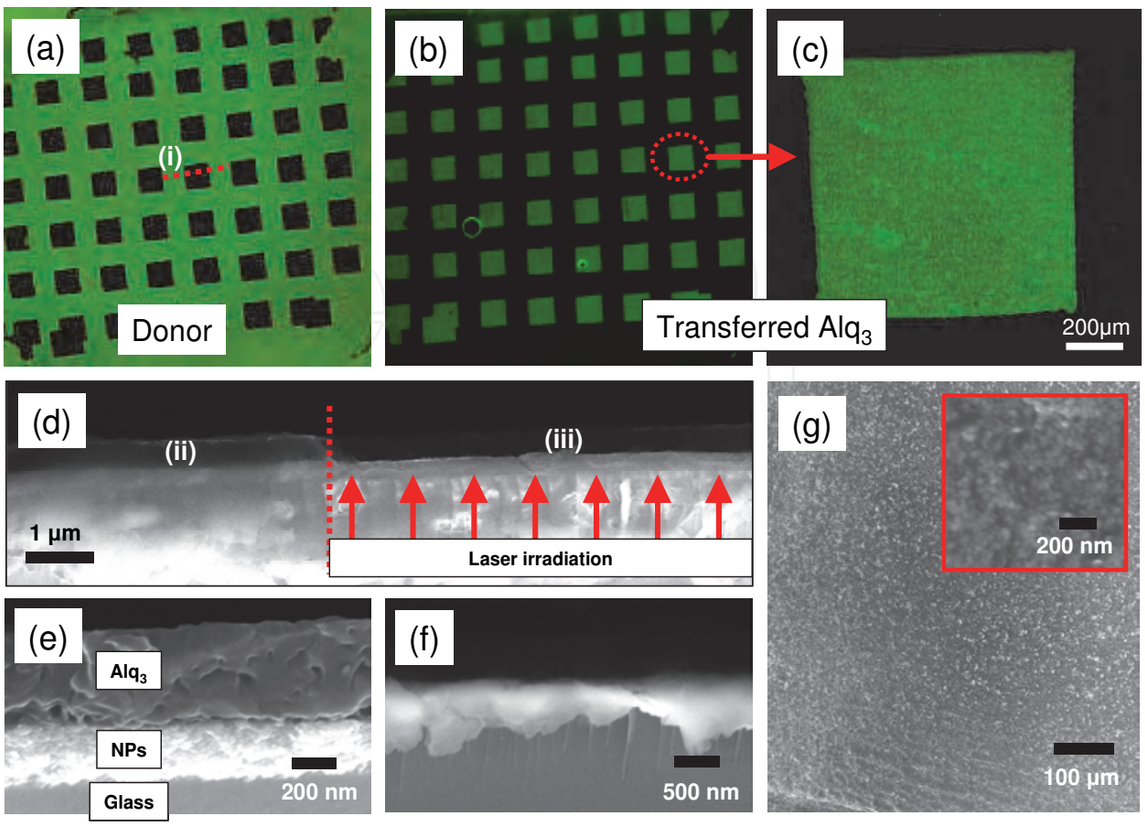
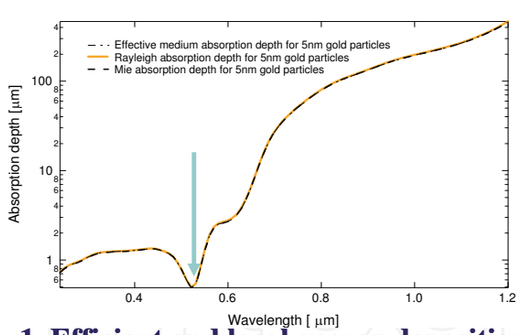


Fig. 7. Fluoresce pictures of (a) a donor substrate and (b) transferred Alq3 patterns (0.9×0.9mm² squares with 2 mm pitch) on a PDMS/glass substrate under UV lamp illumination. (c) Magnified fluoresce micrograph of individual transferred Alq3 pattern under UV lamp illumination. (d) SEM cross sectional picture near laser edge along line (i) in (a). Magnified SEM cross sectional pictures of original donor with Alq3/Ag NPs/glass structure before laser transfer and of (f) donor after laser transfer at (ii) and (iii) in (d) respectively. (g) SEM top view picture of transferred Alq3/Ag on PDMS/glass substrate. Inset is the magnified SEM top view picture. (Ko et al. 2008)

Nanomaterials exhibit remarkable properties that may be substantially different from those observed in the bulk counterparts due to the large surface-to-volume ratio, large surface energy, and the confinement of molecules, atoms, and electrons within a small spatial region. Note that the typical laser fluence (0.07-0.12 J/cm²) used for NELT based on Ag NPs is considerably lower than the reported ablation threshold (Bäuerle et al. 2000) for metal films (1–10 J/cm²) for nanosecond laser irradiation at visible wavelength.

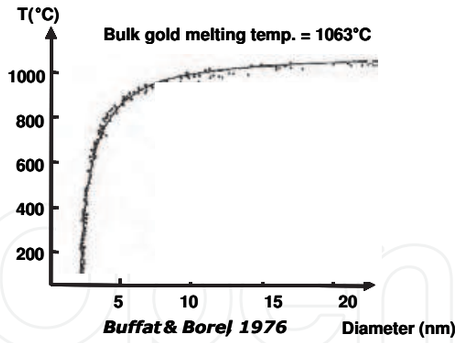
Proper selection of nanoparticle size, size distribution, as well as the material type may allow highly efficient laser energy coupling via tuning to an absorption peak. Noble metal NPs such as Au and Ag exhibit strong absorption peaks in the visible wavelength region that are typically not observed in the bulk materials due to surface plasmon oscillation modes of conduction electrons in the nanoparticles (Figure 8). Additionally, enhanced electric fields between nanoparticles may contribute to more efficient energy absorption mechanisms. (Ko et al. 2006)



1. Efficient and local energy deposition

->Strong absorption (Rayleigh scattering regime + surface plasmon)

2. Low ablation threshold



Thermodynamic property :

size dependent melting temperature depression

Fig. 8. Optical property and melting temperature depression of metal nanoparticles.

For efficient energy absorption, the deposited energy may be more confined to the laser focal zone due to the reduced thermal diffusion of nanoparticle thin films. This implies that the relatively lower thermal conductivity of a nanoparticle thin film reduces the rate of lateral energy dissipation, thereby facilitating the heating, evaporation and transfer processes. The low thermal conductance of the alkanethiol SAM is due to the vibrational mismatch between the nanoparticle solid core and the surface coating as reported by several researchers. (Wilson et al. 2002, Wang et al. 2006)

The melting temperature depression may also enable ablation driven by the nanomaterial melting and vaporization at much lower laser energies than for bulk materials. (Figure 8) Upon reaching the SAM desorption temperature (typically at about 150~250°C), the SAM coating may be removed. At this stage, molten nanoparticles agglomerate to form larger particles or are expelled by the pressure built up from the volatile species expansion attributed to desorbed SAM, vaporized residual organic solvent and trapped gases. Additionally, due to the presence of the SAM coating, the nanoparticles may be held together by weak physical van der Waals force compared with the strong metal bonding in thin metal film. (Altman et al. 2005) Therefore, the expulsion may be enhanced by the relatively weak bonding between the nanoparticles.

Due to the combined aforementioned effects, NELT results in laser transfer at relatively smaller laser energy with minimal thermal damage to the target OLED material. The Alq3 layer shows strong decrease in fluorescence if the temperature exceeds approximately 300°C. Therefore, the Alq3 layer does not encounter higher temperatures during the laser transfer process.

Figures 9 and 10 illustrate that this process can fabricate Alq3 patterns of arbitrary shape. Figure 9 shows step and pixelized transfer of Alq3 patterns by irradiation of a large area homogenized laser beam (of ~mm size) while figure 4 depicts Alq3 patterning by tightly focused Gaussian laser beam (<10μm). Figure 9 displays photographs of the fluorescing transferred Alq3 patterns on a PDMS/glass substrate under UV lamp illumination. The green letters (a) "UCB", (e) "LTL" and the star shapes correspond to regions where the laser irradiation resulted in the transfer of the Alq3 material from the donor substrate to the receptor substrate. The "UCB" and "LTL" letters were formed from combining the 0.9×0.9

mm2 squares with single laser pulse (0.072 J/cm²). The lines of stars indicated at (a-i,ii) and (e-i,iii) were patterned using a homemade aluminum mask on a glass slide (placed before the objective lens for scaling down the projection of the mask at 1:10 reduction) using the same pulse energy as for the above letters. Figures 9(b-d), (f-h) show the magnified fluorescence micrograph of individual transferred Alq3 pattern of star shapes (b,f) and letters (c,d,g,h). The bubbles appearing in Figure 9(a,e) are in the PDMS adhesion layer and not a result of the Alq3 laser transfer process. In all cases, the fluorescence of the transferred Alq3 is strong, indicating no damage during the transfer process. Additionally, the edges of the transferred patterns are sharp and well defined, confirming good spatial control of the transfer.

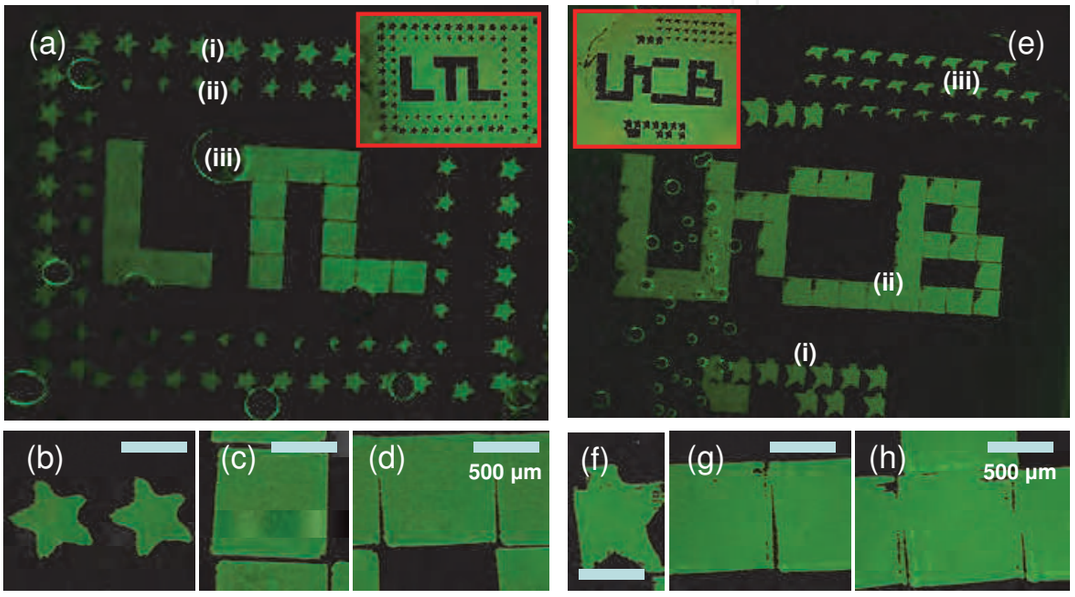


Fig. 9. Step and irradiation of large sized homogemized beam. Fluoresce pictures of transferred Alq3 patterns on a PDMS/glass substrate under UV lamp illumination. (a) (i) star shapes made by homemade mask and (ii~iii) "LTL" letters made by 0.9 × 0.9 mm2 squares. Magnified fluoresce micrograph of individual transferred Alq3 pattern of (b) star shapes, (c~d) letters under UV lamp illumination. (e) (i) star shapes made by homemade mask and (ii~iii) "UCB" letters made by 0.9 × 0.9 mm2 squares. Magnified fluoresce micrograph of individual transferred Alq3 pattern of (f) star shapes, (g~h) letters under UV lamp illumination. Small circles are the bubbles formed in PDMS layer and has nothing to do with current process. (Ko et al. 2008)

Figure 10 shows fluorescence pictures of transferred Alq3 patterns on a PDMS/glass substrate by raster scanning tightly focused Gaussian laser pulses. Alq3 micro dot arrays were transferred by (a,b) 5X, (c) 20X, (d) 50X objective lens focusing. A range of sizes of Alq3 micro dot arrays ((a,b) 20~25 μm (5X), (c) 5 μm (20X), (d) 3 μm (50X)) could be transferred via the objective lens focusing. Alq3 micro dot arrays were smaller than the original focused laser beam size (5X: 10 μm, 20X: 3 μm, 50X: 2 μm). Instead of using single laser irradiation of homogenized large area beam to transfer 1 mm2 square patterns as shown in Figure 7, square patterns of similar size and quality could be achieved by raster scanning a laser beam focused by a 5X objective lens along the arrow direction (Figure 10(d)).

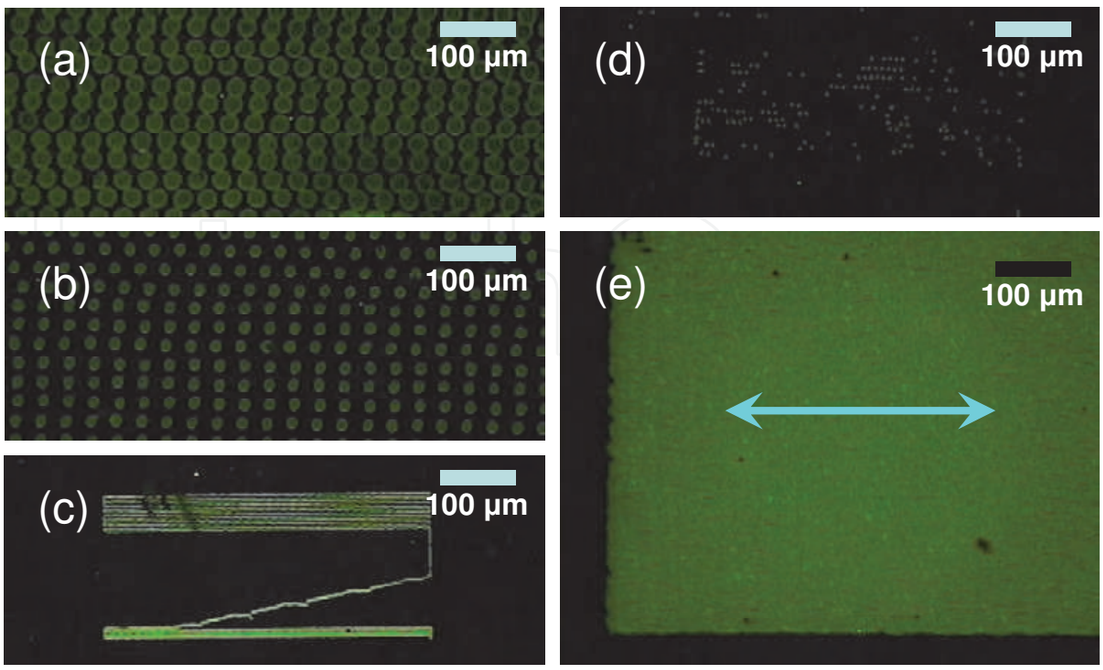


Fig. 10. Raster scanning of focused Gaussian beam. Fluoresce pictures of transferred Alq3 patterns on a PDMS/glass substrate under UV lamp illumination. Alq3 dot arrays transferred by (a,b) 5X, (c) 20X, (d) 50X objective lens focusing. 1 mm^2 square by raster scanning of focused laser with 5X objective lens. Arrow indicates laser spot scanning direction. (Ko et al. 2008)

In summary, the nanomaterial enabled laser transfer (NELT) method was demonstrated to directly pattern and transfer Alq3 through laser absorbing layer engineering. The combined effects of melting temperature depression, lower conductive heat transfer loss, strong absorption of the incident laser beam, and relatively weak bonding between nanoparticles during laser irradiation result in the transfer of patterns with very sharp edges at relatively lower laser energy than commonly used, thus inducing minimal damage to the target OLED material with no evidence of cracks. This technique is not limited to the current specific combination of the Ag NPs with alkanethiol SAM protective layer and the utilized laser wavelength, but can be applied to a broad range of laser wavelengths with proper selection of nanoparticle size and size distribution, as well as the material type. Additionally, NELT may be particularly advantageous for the mass production of temperature sensitive devices.

2.5 Self Assembled Monolayer assisted Nanomaterial Enabled Laser Transfer [SAM-NELT]

NELT process could demonstrate the OLED material pixel transfer. The NPs were used to facilitate the OLED material transfer at low laser energy. Some part of NPs will transferred from donor substrate on OLED material surface. The transferred NPs may be beneficial for some points such that they can be used for metal electrode or may enhance the luminescence by surface plasmon. However, for some application, there is a strong needs for modified NELT process without using NPs. In this section, self assembled monolayer assisted NELT (SAM-NELT) is introduced for variant of NELT process.

Figure 11 illustrates the schematics of NELT process (Figure 11(a)) and the two types of donor multilayer (figure 11(b)). Either a large area homogenized beam or a tightly focused Gaussian Nd:YAG pulsed laser beam (wavelength = 532 nm, pulse width = 5 ns FWHM) were applied normal to the donor substrate which was composed of three parts; transparent substrate (borosilicate glass slide) / laser-to-heat conversion layer (nanomaterials) / target material (OLED material). The applied laser induces the local heating of laser-to-heat conversion layer and the transfer of the OLED material patterns onto the flexible receptor substrate. In this experiment, two types of SAM (self assembled monolayer, Alkanethiol) coated nanomaterials were used as the laser absorbing and dynamic releasing layer: SAM coated Ag nanoparticle thin film (type I) or SAM layer coated Au thin film (type II). SAM protected Ag nanoparticles (30~40 nm sized) were spin-coated on the glass substrate to form a 100~200 nm thin film and SAM coated Au thin film (100nm on 5nm Cr layer) was prepared by e-beam evaporation and subsequent SAM coating. The homogenized Nd:YAG laser beam cross section was shaped to a 0.9 × 0.9 mm^2 flat top beam profile of good spatial uniformity by a micro-lens laser beam homogenizer while the tightly focused laser beam size had a 2~10 μm (FWHM) $1/e^2$ diameter Gaussian profile. The applied laser fluence was around 0.05~0.15 J/cm^2 for type I donor with SAM coated Ag nanoparticle thin film and 0.01~0.05 J/cm^2 for type II donor with SAM coated Au thin film. The optical property measurement by spectroscopic ellipsometry) indicates the nanoparticle thin film has strong absorption around 530 nm facilitating highly efficient Nd:YAG laser absorption to the NPs laser while the polymer material exhibits little absorption. The target OLED material were 1) green fluorescent monomer: tris-(8-hydroxyquinoline)Al (Alq3) layer (200~300 nm) deposited by a resonant infrared pulsed laser deposition (RIR-PLD) technique (Dubb et al, 2001) and 2) blue fluorescent polymer: PFO layer (100~300nm) deposited by spincoating. RIR-PLD was done by Free-Electron Laser (FEL) with the wavelength of 6.67 μm, which corresponds to the resonance peak of Alq3 absorption in IR, 5μs pulse width, and fluence of 1.5 J/cm^2 at 30 Hz for 2-3 minutes. The donor substrate was then placed on top of the receptor substrate with a small gap or intimate contact with the acceptor substrate in ambient air environment. The receptor substrate was a thin PDMS layer.

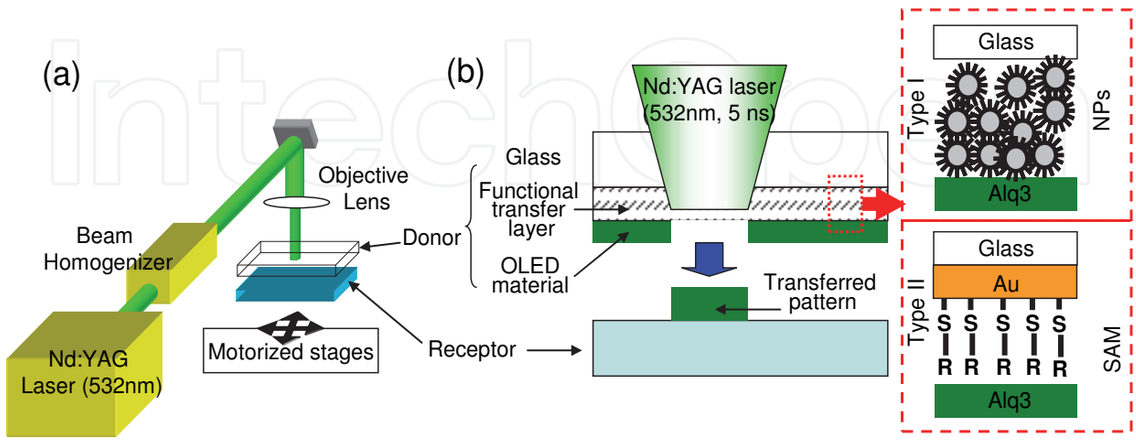


Fig. 11. (a) Schematic diagram of experimental set up for a nanomaterial enabled laser transfer with a homogenized Nd:YAG laser. (b) Magnified schematic illustration of the laser transfer process and the two types of donor multilayer. (Ko et al. 2010)

For certain applications, these nanoparticles transferred with the OLED material can be regarded as the contaminants. This side-effect can be removed by using type II donor. The micrographs of individual transferred Alq3 and PFO patterns from type II donor show successful OLED material transfer without damaging or transferring of Au thin film.
Transferred OLED material pattern can be controlled by laser scanning or laser beam shaping. Alternatively, selective transfer can be induced by pre-patterning of laser absorbing layer. Figure 12 shows the schematics and the fluorescent pictures of transferred Alq3 pattern on the PDMS substrate (Fig. 12(b)) and the donor substrate (Fig. 12(c)). Laser was scanned for large area with constant laser energy, and the transfer happened only for the area with pre-patterned type II donor (SAM coated Au thin film).

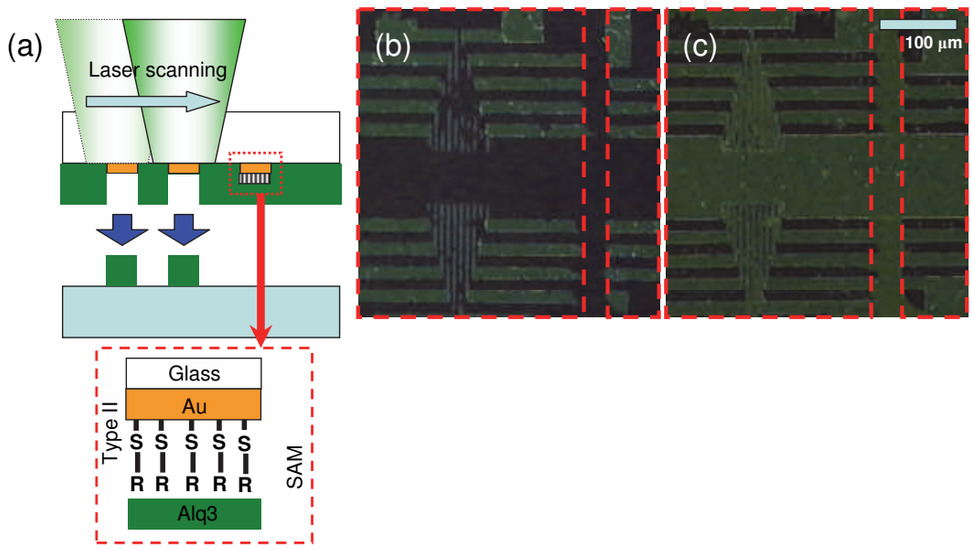


Fig. 12. (a) Schematic diagram of selective NELT process for a pre-patterned type II donor substrate. (b) Fluorescent images of (b) transferred Alq3 patterns on a PDMS film and (c) donor substrate after NELT process. (Ko et al. 2010)

3. Conclusion

Organic light emitting diode (OLED) displays have a number of desirable features such as high contrast and brightness, wide color range, thin structure and light weight, among others and OLED displays have several manufacturing requirements such as large area scalability and an increasing push towards smaller feature sizes, tighter feature shape control, high yield and low cost. However, traditional lithography and thermal evaporation deposition techniques have significant disadvantages, including the need for masks that are typically difficult to make to the required specifications at a reasonable price. Vacuum-processable OLEDs have been patterned mostly by deposition through a shadow mask or fine-metal mask (FMM). Deposition can be accomplished either as a conventional physical evaporation or organic vapour phase deposition (OVPD), but FMM-related patterning issues are largely independent of the deposition technique. Remaining FMM patterning issues include difficulty of fabricating high resolution masks for large-area displays, mask lifetime and cleaning, particle contamination, and thermal expansion effects. Therefore, there is a strong need to develop a novel process instead of complex modification of

conventional vacuum deposition and photolithography based processes. OLED display manufacturing employs direct write techniques for patterning the various materials. Examples of OLED material direct write technologies include ink jet printing, screen printing and laser induced forward transfer (LIFT). Solution processible direct write technologies such as inkjet printing and screen printing are subject to a number of limitations such as the need for solvent removal and contamination into the deposited material. Additionally, the minimum feature size is heavily influenced by the properties of the fluid used to deliver the material of interest and multilayer structure fabrication is difficult. In this chapter, unconventional OLED material direct patterning and transfer methods especially laser based forward transfer and patterning approaches were presented as promising potential alternative to conventional OLED fabrication methods.

4. Acknowledgment

The authors would like to thank Dr. H.K. Park of AppliFlex LLC, (CA, USA) for his advices and supports. The authors also would like gratefully acknowledge the financial supports to KAIST by the Industrial Strategic Technology Development Program from the Korea Ministry of Knowledge Economy (Grant No. 10032145), the National Research Foundation of Korea (Grant No. 2010-0003973), the cooperative R&D Program from the Korea Research Council Industrial Science and Technology (Grant No. B551179-10-01-00), and the support to the University of California, Berkeley by the NSF STTR (Grant No. 0930594) through Appliflex LLC, CA, USA.

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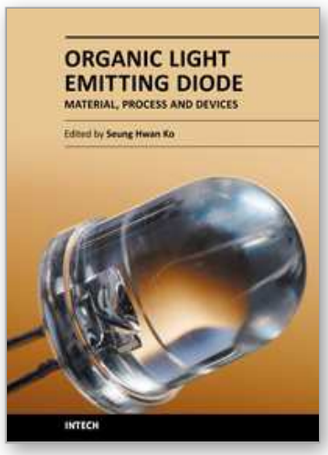

Organic Light Emitting Diode - Material, Process and Devices

Edited by Prof. Seung Hwan Ko

ISBN 978-953-307-273-9
Hard cover, 322 pages
Publisher InTech
Published online 27, July, 2011
Published in print edition July, 2011

This book contains a collection of latest research developments on Organic light emitting diodes (OLED). It is a promising new research area that has received a lot of attention in recent years. Here you will find interesting reports on cutting-edge science and technology related to materials, fabrication processes, and real device applications of OLEDs. I hope that the book will lead to systematization of OLED study, creation of new research field and further promotion of OLED technology for the bright future of our society.

How to reference

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Seung Hwan Ko and Costas P. Grigoropoulos (2011). Unconventional, Laser Based OLED Material Direct Patterning and Transfer Methods, Organic Light Emitting Diode - Material, Process and Devices, Prof. Seung Hwan Ko (Ed.), ISBN: 978-953-307-273-9, InTech, Available from: http://www.intechopen.com/books/organic-light-emitting-diode-material-process-and-devices/unconventional-laser-based-oled-material-direct-patterning-and-transfer-methods

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