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Laser-assisted forward transfer of multi-spectral nanocrystal quantum dot emitters

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Abstract
We report in this paper the development of a novel laser-transfer scheme to integrate laterally arrays of light-emitting pixels made of semiconductor nanocrystal quantum dots (NQDs). The nanocrystal composition and size can be tailored such that the luminescence emission of the quantum dots in each device pixel constitutes a distinctive spectral channel of narrow bandwidth. An ultrathin film of photosensitive triazene polymer (TP) has been employed as the sacrificial layer whose decomposition upon UV excitation delivers the bilayer structure of nanocrystal and metal films to the substrates. The ejected plume of the decomposed photosensitive polymer produces a thrust force to ensure the conformal contacts between the NQD layer and the bottom hole transport layer. A 6 × 6 red and yellow matrix with pixel sizes of 800 μm is demonstrated. This technique opens up the possibility of developing small, on-chip light sources featured with multiple wavelength channels over a desired spectral range as well as the flexible substratum.

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

Recently, colloidal semiconductor nanocrystal quantum dots (NQDs) has drawn immense attention in the photonics research community due to their superior optical properties and easy processibility [1–3]. Semiconductor NQDs are nanocrystals that are smaller in size than the diameter of a Bohr exciton in a bulk crystal of the same material. By reducing the size of the nanocrystal core, the quantum confinement of the electronic states in the NQD is increased, with a consequent increase in the exciton energy. In CdSe nanocrystals, for instance, quantum confinement increases the exciton energy from a bulk bandgap of 1.7 eV to any value up to 2.75 eV, and by controlling the particle size during the synthesis, the peak emission wavelength of CdSe(ZnS) core/shell NQDs can be tuned continuously from 470 nm to 650 nm [1, 2]. In addition to the broad wavelength tunability, high fluorescence quantum yield and photochemical stability can be achieved by the careful modification of the nanocrystal surface, which favours the quantum efficiency of the luminescence of the nanoparticles.

The development of low-cost, solution-based synthesis of monodisperse, well-characterized NQD samples has generated a new material set for next-generation light-emitting devices (LEDs). Electroluminescent (EL) devices have been fabricated from thin films of NQDs and exhibit high brightness, narrow spectral full-width at half-maximum (FWHM) bandwidth and flexible substratum [4–10]. Emission of EL devices can easily be tuned by varying the size and/or the material composition of nanoparticles during the synthesis process, while their chemical properties remain largely the same. Therefore, one device fabricating procedure can be adopted for different nanocrystals to produce emissions over a broad wavelength range, covering the visible (0.4–0.8 μm) and near-infrared

(0.8–2.5 μm) regions of the spectrum [4, 7–10] This unique property has made the NQD-based LED a promising candidate for the development of multi-spectral light sources which have potential applications in the fields of colour display and spectroscopic sensing.

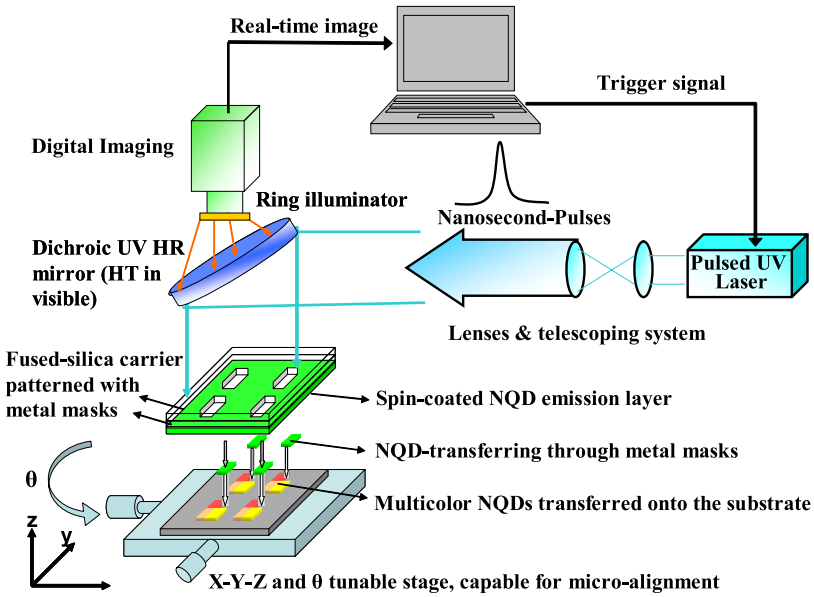
In order to develop LED colour display and on-chip, multi-spectral light sources using NQDs, it is necessary to integrate on the same substrate NQDs of different size and, therefore, of different emission wavelengths. A 'vertical' integration scheme has been proposed and demonstrated recently [11]. The device structure reported consists of two or three layers of NQDs of different diameters, (therefore, of different bandgap energies), with the wide bandgap layers placed over the narrow bandgap layers. Intervening layers of polymers are inserted between NQD layers to prevent the mixing between NQD families. Both the photoluminescence and electroluminescence of the vertically integrated structure exhibit broad emission spectra with multiple wavelength peaks corresponding to the emission wavelength of each component layer. While such a 'broadband' or spectrally engineered device has potential applications in white light emitters for illumination and wavelength code-division multiple accesses for optical communication [12], it is difficult to achieve narrow linewidth emission and broad spectral tunability simultaneously with the vertically integrated LED structures.

A more useful integration scheme is to fabricate arrays of NQD emitters by aligning on a common substrate, side by side, many nanocrystal LEDs of different output wavelengths. In the active region of the arrayed device, both the composition and the size distribution of the NQDs can be tailored such that the light emission from the NQDs in each device constitutes a distinctive spectral channel of narrow bandwidth. When an NQD-LED array consists of multiple spectral channels, its output can be designed to cover a broad spectral regime. Such multi-spectral light-emitting arrays will find potential applications in display technology, analytical spectroscopy, and *in situ* bio/chemical sensors [13, 14]. This paper describes the fabrication of arrayed NQD emitters of dual spectral channels with the technique of laser-assisted forward transfer. The reported work opens up the possibility of developing small, on-chip light sources featured with multiple wavelength channels covering a broad spectral regime as well as the flexible substratum.

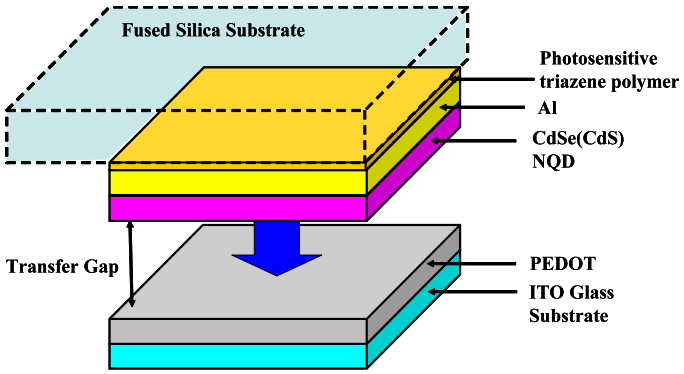
The technique of laser-assisted forward transfer has been developed in the last decade as a direct writing technique to pattern metal powders and ceramic powders onto the surfaces of various types of substrates with micron resolution [15–19]. This technique utilizes a laser transparent fused silica disc, the so-called 'donor substrate', which is coated on one side with a composite matrix consisting of the particle material to be deposited mixed with a laser-absorbing host polymer. Absorption of laser radiation results in the decomposition of the polymer which, when it is exposed to a focused laser beam spot, aids in transferring the solute to an 'acceptor substrate' placed parallel to the matrix surface [18]. The successful transfer process, however, requires that the particle material is robust toward the high-intensity UV exposure during laser ablation of the polymer matrix. While this requirement is often met with metal and ceramic particles, light-sensitive nanoparticles, such as colloidal semiconductor NQDs, are often susceptible to the photocatalytic degradation upon strong UV exposure [20]. In addition, when the transferred NQD layers constitute the active regions of the light-emitting devices, the matrix host polymer involved in the laser transfer introduces contamination to the active region, which will degrade the device performance. Such drawbacks have impeded the adoption of the transfer method to the patterning of semiconductor nanocrystals in fabricating NQD-based photonic devices.

We have developed a new laser transfer scheme where a thin metal film is inserted between a NQD active layer and the polymeric sacrificial layer deposited on the UV transparent donor substrate. During the laser transfer process, the metal–NQD bilayer structure will be forward transferred to the bottom substrate via the photo-induced decomposition of the polymeric sacrificial layer. The metal layer physically separates NQDs from the sacrificial polymers, which prevent NQDs from being contaminated during the transfer process. It also blocks the direct UV exposure over the nanoparticles for any ablation damage. Moreover, this metal layer can be designed to function as the top electrode in an EL-based NQD-LED, making such a transfer scheme compatible with the integral process of the device fabrication. The transfer can be implemented through the UV masks patterned on the donor substrates, which resembles the lithography process. A single exposure to the UV laser light will facilitate the transfer of one type of NQD emitters onto the acceptor substrate. Arrays of NQD emitters of varying NQD sizes and NQD compositions can therefore be integrated on a single chip through multiple-step transfer of metal–NQD bilayers originally prepared on a set of donor substrates.

A detailed description of the laser-assisted transfer experiment is as follows (figure 1(a)): laser-transparent fused silica discs were, first, coated with ultrathin (∼40 nm) films of photosensitive triazene polymer (TP). The coated discs served as donor substrates over which an array of aluminium dots, about 200 nm thick and 800 μm in diameter, was deposited through a shadow mask with thermal evaporation. This was followed by spin-casting of the CdSe(CdS) solution over those aluminium electrodes, acting as the active layer of the emitter structure. The typical thickness of the NQD layer was between 50 and 200 nm. By varying the size and composition of the NQDs in the solution cast process, a set of donor discs was created, each carrying a 'monochromatic' array of NQD-emitter pixels characterized with a distinctive emission wavelength. Upon the laser transfer process, the donor disc was exposed to a pulsed UV laser beam. An excimer laser (Lambda Physik Compex102) was used to produce 193 nm UV pulses at an output fluence of 30 mJ cm^{-2}. Laser ablation resulted in the rapid decomposition of the photosensitive TP film, which released the Al–NQD bilayer pixels from the donor disc. The gaseous ablation products of TP propelled the released pixels toward an acceptor substrate placed in close proximity to the donor disc. Alignment of the transferred array pattern with the acceptor substrate was achieved by *in situ* imaging and controlled x–y plane translation of the acceptor substrate, as shown in figure 1(b). In our study, the acceptor substrates were glass wafers coated with indium–tin oxide (ITO) serving as transparent bottom electrodes in the NQD emitter structure. To achieve interfacial adhesion



(a)



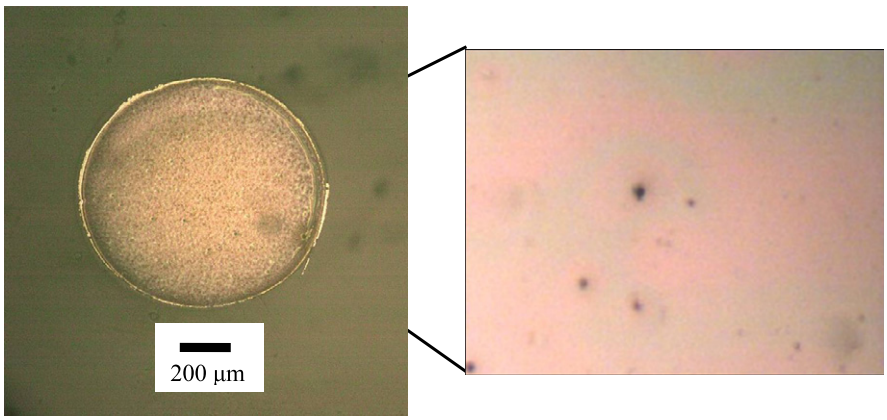
(b)

Figure 1. (a) Schematic diagram of the experimental setup for the laser-assisted forward transfer of multi-spectral nanocrystal quantum dot emitters; (b) schematic illustration of the laser transfer process.

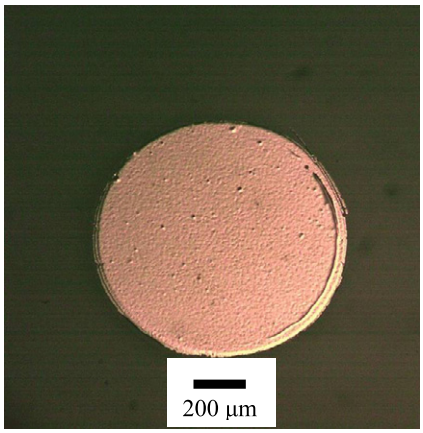
between the transferred pixels and the acceptor substrate, a thin (∼40 nm thick) interfacial layer of conductive polymer, poly-3,4-Ethylenedioxythiophene (PEDOT), were spin coated over the ITO electrodes of the acceptor substrate right before the laser transfer. When TP was ablated with a pulsed laser beam, the ejected plume of decomposed gaseous monomers produced a thrust force to ensure conformal contacts between the top NQD layer and the bottom PEDOT layer, similar to that of the microcontact printing process [21, 22]. In an NQD-EL device, the PEDOT layer could also facilitate hole transport between quantum dots and bottom ITO electrodes. By this approach, a multi-step transferring process could produce arrayed NQD-emitter chips with multiple wavelength channels.

The conditions of the laser transfer process have been studied for their influences on the morphology of the deposited NQD layer. Figure 2 shows the photomicrographs of the front and back surfaces of an 800 μm-diameter pixel of a Al–NQD bilayer structure transferred onto an ITO glass substrate. The thicknesses of the NQD and Al layers are ∼50 nm and ∼200 nm, respectively. It is evident from the microphotograph that, other than a few large dots, the surface morphology of the transferred NQD layer is quite uniform over regions as large as hundreds of micrometre across. There is no noticeable occurrence of aggregation of the transferred nanoparticles. The residual roughness was found to be due primarily to the imperfect surface flatness of the underlying substrate.

It is found, in the experiments, that two factors played key roles in avoiding the random lateral displacements of the released NQD pixels during the transfer process, i.e. the gap distance between the donor disc and the acceptor substrate and the critical thickness of the TP sacrificial layer. The microscopic study on the nanosecond-pulsed laser ablation



(a)



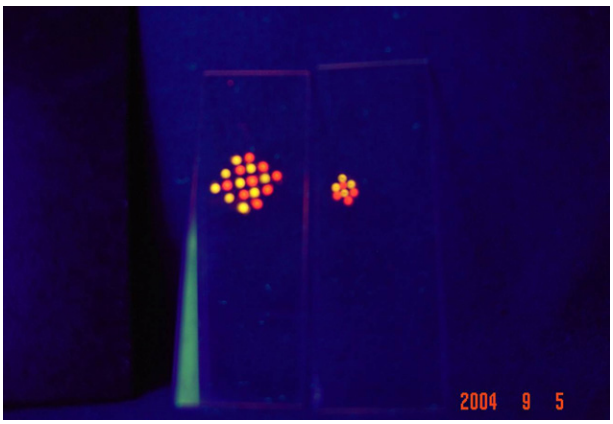
(b)

Figure 2. Photomicrographs of the (a) front and (b) back side of the transferred nanocrystal/metal bilayer structure.

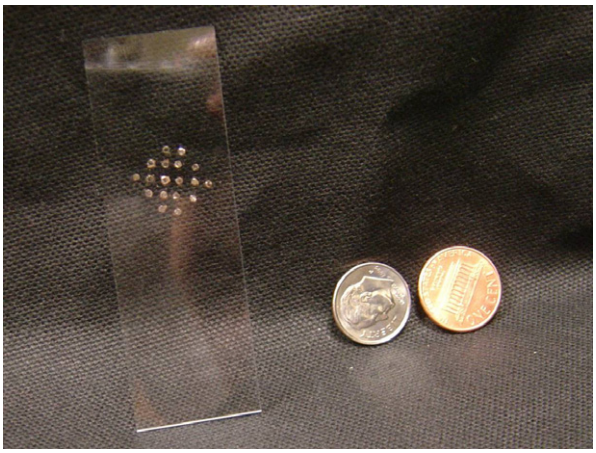
of a photosensitive triazene polymer has revealed that the ejection of the decomposed gaseous monomers produces blast shock waves in the surrounding media whose propagation matches a planar blast-wave model, which is indicative of the microexplosion nature [23–26] The reaction occurs instantaneously, whereas the high-pressure gas expands at a large velocity and acts as a piston, pushing this NQD/metal bilayer pixels outward. Any minor asymmetries involved in the released structures, as well as in the pattern alignment prior to the transfer process, will lead to translational and rotational motion of the released pixels and cause misalignments in the final transferred patterns. In order to circumvent this difficulty, the surface of the donor disc was positioned in closed proximity ($\leqslant 1$ μm) to the substrate during the transfer process to minimize the vertical transport distance of the NQD/metal pixel. The thickness of the sacrificial TP layer was also tailored to control the magnitude of the microexplosion intensity such that the thrust force that was created was just large enough to propel the released structures down to the substrate without any extra damage incurred by the released components.

Figure 3 shows a 6 $\times$ 6 matrix of alternating pixels composed of 5 nm-diameter CdSe(CdS) NQDs (yellow) and 6 nm-diameter NQDs (red) which was patterned on glass substrates with the laser transfer technique. Images were taken under both UV and room-light illumination conditions. No degradation was observed in the luminescent efficiencies of the transferred NQDs, as shown in figure 4. The fluorescence spectra of the transferred NQDs were identical to that of the NQD layers deposited on the fused silica-donor substrate prior to the transfer process. It is evident that both the packing density and the structure of NQDs are maintained during the laser transfer process. Successful transfer of NQD-emitter arrays has been accomplished for a pixel size varying between 300 μm and 1 mm in diameter, which was limited by the resolution of the alignment optics used in the forward transfer setup of our lab.

It is noted that the 'distorted shape' of some pixels observed in the room-light image (figure 3(b)) is simply a visual artifact caused by the nonuniform illumination condition. In fact, the circular pixel shape is largely retained during the forward transfer process. While the diameters of the transferred pixels were limited between 300 μm and 1 mm in our experiments, we predict that NQD-emitter pixels of much smaller size can be patterned into multicolour arrays with the aforementioned technology upon the improved resolution of the alignment optics in the laser transfer setup. Using the similar transfer technique of direct laser-writing, Wu *et al* reported the possibility of depositing pixels of biomaterials,



(a)



(b)

Figure 3. Pictures of an ITO glass plate carrying a 6 × 6 matrix of alternating pixels composed of 5 nm-diameter CdSe(CdS) NQDs (yellow) and 6 nm-diameter NQDs (red) under (a) UV illumination and (b) room light illumination. The nanocrystal emitter matrix was patterned over the ITO glass plate by the laser transfer process.

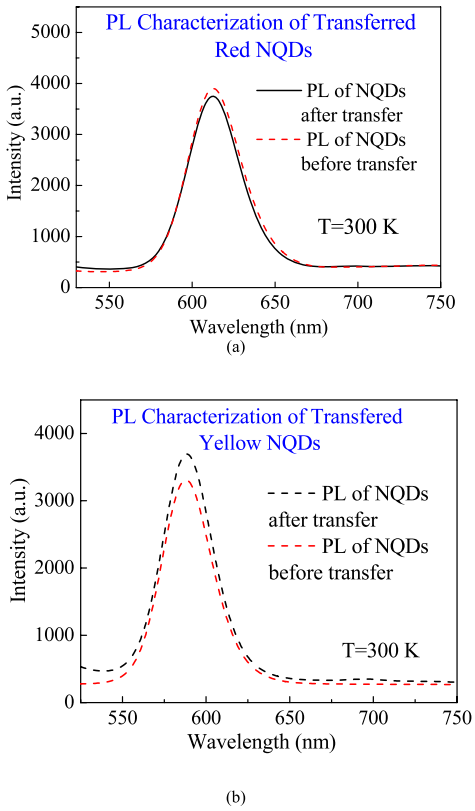


Figure 4. Photoluminescence spectra of (a) 5 nm nanocrystals and (b) 6 nm nanocrystals prior to and after the laser transfer process, respectively. Both PL spectra were recorded under the same experimental conditions, i.e. with the same excitation power.

with a spatial resolution of 50 μm × 50 μm and accuracy better than 10 μm [19]. As the size of the pixels shrinks, however, the problem of random lateral displacements of the transferred pixels will become more prominent, because the higher possibility of having defective asymmetry in smaller pixels, along with the reduced mass of the transferred substance, could lead to severe deflection of the pixel releasing path, as analysed above. The capability of precisely controlling the array fabrication conditions, including the laser fluence, the sacrificial layer thickness, the gap distance between the donor disc and the acceptor substrate, and the metal–NQD bilayer processing, will eventually determine the resolution and accuracy of the laser-assisted forward transfer process.

In summary, we have developed a novel laser-assisted transfer scheme to integrate laterally arrays of semiconductor NQD pixels of different NQD size and composition, which could potentially lead to NQD-LED based multi-spectral light sources. An ultrathin film of photosensitive triazene polymer has been employed as the sacrificial layer whose decomposition upon UV excitation delivers the bilayer structure of NQDs and metal films to the accepting substrates. The ejected plume of the decomposed photosensitive polymer produces a thrust force to ensure the conformal contacts between the NQD layer and the bottom hole transport layer. A 6 × 6 red and yellow matrix with pixel sizes of 800 μm is demonstrated. This technique is scalable for the fabrication of NQD arrays of pixel sizes varying over a large range.

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