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Contact Printing of Quantum Dot Light-Emitting Devices

LeeAnn Kim,† Polina O. Anikeeva,† Seth A. Coe-Sullivan,‡ Jonathan S. Steckel,‡ Moungi G. Bawendi,*§ and Vladimir Bulovic*,†

Laboratory of Organic Optics and Electronics, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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ABSTRACT

We demonstrate a solvent-free contact printing process for deposition of patterned and unpatterned colloidal quantum dot (QD) thin films as the electroluminescent layers within hybrid organic-QD light-emitting devices (QD-LEDs). Our method benefits from the simplicity, low cost, and high throughput of solution-processing methods, while eliminating exposure of device structures to solvents. Because the charge transport layers in hybrid organic/inorganic QD-LEDs consist of solvent-sensitive organic thin films, the ability to avoid solvent exposure during device growth, as presented in this study, provides a new flexibility in choosing organic materials for improved device performance. In addition, our method allows us to fabricate both monochrome and red—green—blue patterned electroluminescent structures with 25 µm critical dimension, corresponding to 1000 ppi (pixels-per-inch) print resolution.

Exceptional luminescent properties of colloidal QDs\(^1\) such as the narrow emission spectra tunable throughout the entire visible spectrum (corresponding to highly saturated emission colors) and the high photoluminescence efficiencies suggest the use of QD films in electroluminescent devices and pixilated full-color displays. The pioneering demonstrations of QD applications in light-emitting devices (LEDs) utilized conjugated polymer—QD blends as emissive layers and exhibited low efficiencies as compared to polymer LEDs.\(^2,3\) The subsequent significant increase in the external quantum efficiency (EQE) (reaching EQE of 0.5% to 2%\(^4-6\)) of hybrid organic/inorganic QD-LEDs was demonstrated in structures that used a single monolayer of QDs\(^4\) surrounded by organic transport layers. The use of QD monolayers minimized the negative impact of QD charging and resistive power losses associated with poor QD-to-QD charge transport,\(^8,9\) characteristic of the earlier devices that utilized QD multilayers.\(^10\) These technical advances highlighted the need for development of a reproducible method of formation of close-packed QD monolayers, with a preference of generating laterally patterned QD films, as would be needed in full-color pixilated structures.

Large area (several cm\(^2\)) QD monolayers can be assembled out of solution, either by Langmuir—Blodgett\(^11,12\) or by spin-casting (phase segregation)\(^5\) techniques. The critical limitation of the Langmuir—Blodgett assembly technique is in its low throughput and cumbersome implementation that appears incompatible with industrial-scale production. The spin-casting assembly technique has two critical limitations: (1) it cannot be applied to patterning of QD monolayers, and (2) it places solvent compatibility requirements on the device fabrication process. Consequently, adaption of the technique to the fabrication of active electronic devices, such as QD-LEDs requires the devices to be designed around the deposition technique that demands solvent compatibility and can lead to nonideal device structures of inferior performance. The lack of simple methods for in-plane patterning of pixilated QD-LEDs has largely been ignored in published literature\(^13\) and is the topic of the present work. In this Letter we demonstrate that contact printing\(^12,14\) can be used to deposit patterned, solvent-free QD monolayers. We demonstrate the flexibility of the approach and its functional use by inserting patterned and unpatterned QD monolayers into active QD-LED structures.

The QD printing process follows the steps schematically shown in Figure 1: (1) poly(dimethylsiloxane) (PDMS) is molded using a silicon master; (2) resulting PDMS stamp is conformally coated with a thin film of parylene-C, a chemical-vapor deposited (CVD) aromatic organic polymer (chemical structure is shown in the inset of Figure 2); (3) parylene-C coated stamp is inked via spin-casting of a solution of colloidal QDs suspended in an organic solvent;
after the solvent evaporates, the formed QD monolayer is transferred onto the substrate (e.g., on top of the first few layers of a multilayer device) by contact printing.

Chemical compatibility between the organic solvents used in QD processing and the elastomer stamp critically influences the QD film morphology and, consequently, QD-LED performance. Previously, it has been shown that QDs can form continuous close-packed monolayers upon spin-casting and phase separation from chloroform or chlorobenzene solutions. These solvents are compatible with a variety of hydrophobic organic ligands used for QD surface passivation during organometallic synthesis. However, a plain PDMS surface is chemically incompatible with chloroform solutions of QDs, which is manifested in nonuniform QD films, caused by chloroform dewetting from PDMS during spin-casting. Figure 2a shows the atomic force microscope (AFM) image of a QD film printed onto N,N'-bis(3-methylphenyl)-N',N'-bis(phenyl)benzidine (TPD) underlayer using a plain PDMS stamp. The film is discontinuous and exhibits morphology characteristic of spinodal dewetting. The peak-to-peak roughness of QD films in this case is >160 nm and rms is >20 nm, too rough for QD-LED fabrication. The characteristic organic charge transporting layers that are on the order of 50 nm in thickness are likely to be electrically shorted by the rough QD layers, yielding inoperable devices.

We find that coating the elastomer stamp with parylene-C results in a chemical surface, which is compatible with spreading of colloidal QDs solvated in chloroform. The contact angle measurements show that chloroform wets the parylene-C surface more efficiently than plain PDMS as indicated by the decrease in the contact angle from 28° ± 1° for chloroform on plain PDMS to 6° ± 1° for chloroform on parylene-C-coated PDMS. Chloroform evaporates during the spin-casting of chloroform-solvated QDs on parylene-C-coated PDMS, leaving a monolayer of QDs in contact with the parylene-C surface.

Parylene-C is an aromatic polymer; therefore, its surface is suboptimal for minimizing the surface energy of the QD monolayer, since QDs are generally capped with aliphatic organic ligands (such as trioctylphosphine and oleic acid). The aromatic parylene-C is therefore a good release layer for the aliphatic-capped QDs and facilitates their transfer from the PDMS stamp onto the substrate during the printing process. If instead of parylene-C we employed an aliphatic surfactant on the PDMS stamp, we expect that ensuing strong interaction between QDs and a stamp surface would impede QD release.

AFM image in Figure 2b shows a close-packed monolayer of QDs printed onto TPD film using a parylene-C-coated PDMS stamp. Peak-to-peak roughness of ~5 nm indicates a controlled deposition of a single QD layer. Low rms ≈0.5 nm enables these films to be used in thin (<100 nm thick) hybrid optoelectronic devices. The height distribution analysis of AFM images allows us to determine the number of QD layers deposited via contact printing, which we then use to precisely tune the concentration of QD solution needed.
Figure 3. (a) Electroluminescent red and green QD-LED pixels are fabricated on the same substrate. A blue pixel is the result of TPD emission in the area where QDs were not deposited. (b) Electroluminescent QD-LED pixel is patterned with 25 µm wide stamp features. (Bias voltage is 5 V.) (d) Schematic diagram shows the structure of a QD-LED with an emissive layer consisting of 25 µm wide stripes of green and red QD monolayers. (d) Electroluminescence (EL) of the structure shown in (c) at 7 V of applied bias. Blue emission is due to TPD hole-transporting underlayer. The background TPD emission is not present in the image (b) due to lower applied bias. Corresponding EL spectra can be found in the Supporting Information.

to achieve smooth close-packed QD monolayers (see Supporting Information).

Figure 3a shows the application of the contact printing to fabrication of multiple QD-LED colors on the same substrate. QD-LED structure consists of a transparent indium tin oxide (ITO) anode coated with a hole injecting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT:PSS, followed by 40 nm thick TPD hole transporting layer (HTL), printed QD monolayer, 15 nm thick 3,4,5-triphenyl-1,2,4-triazole (TAZ) hole blocking layer, 25 nm thick tris(8-hydroxyquinoline) (Alq3) electron transporting layer (ETL), and 100 nm thick Ag/Mg cathode with a 20 nm thick Ag protective overlayer. The red (CdSe/ZnS core—shell15) and green (ZnSe/CdSe/ZnS core—double shell16,17) QDs are separately printed onto blanket TPD film, and the structure is completed by blanket deposition of the remaining charge transport layers. The red and green pixels exhibit electroluminescence (EL) solely due to QD emission, while a blue pixel is the result of TPD EL in the absence of QDs.

In panels b and d of Figure 3, we demonstrate patterning of close-packed, monochrome (b) and multicolor QD-LED pixels (d) as small as 25 µm (1000 dpi). We use elastomer stamps with a relief pattern to deposit the 25 µm wide intersecting stripes of red and green QD monolayers in a QD-LED structure shown in Figure 3c. EL of red and green QDs and blue TPD is simultaneously observed when the QD-LED is biased at 7 V. This demonstration presents the first use of contact printing of QDs in the fabrication of patterned EL devices, a critical step toward the realization of pixilated, full color, high-resolution QD-LED displays.

The solvent-free deposition of the QD monolayers is compatible with a wide variety of organic semiconductors that are not compatible with solution processing methods. Figure 4a shows red (CdSe/ZnS core—shell15), green (ZnSe/CdSe/ZnS core—double shell16,17), and blue (CdS/ZnS core—shell18) QD-LED pixels fabricated in the identical device structure shown in Figure 4b, in which wide band gap organic semiconductor, 4,4′-N,N′-dicyanobiphenyl (CBP), replaced TPD as a hole transport material. The wide band gap of CBP contributes to more efficient charge and exciton confinement, and an improvement in color saturation of the QD-LEDs, yielding CIE coordinates (0.66, 0.34), (0.21, 0.70), (0.18, 0.13) for the red, green, and blue QD-LEDs, respectively (shown in Figure 4d), with corresponding EQEs of 1.0%, 0.5%, and 0.2% at video brightness (~100 cd/m²). The normalized EL spectra are shown in Figure 4e, with the spectra of green and red QD-LEDs solely due to the QD emission and blue QD-LED EL spectrum showing a minor contribution from organic thin film EL. EQE and current—voltage characteristics for QD-LEDs in Figure 4 are available in the Supporting Information.

Contact printing can also be used to create mixed-color and white QD-LEDs, since this method is compatible with a variety of colloidal QDs synthesized via different procedures and passivated by different organic ligands. Using the printing method, in recent publications we demonstrated record EQE of 2.3% for red19 0.65% for green6,7 and 0.35% for blue6,7 printed QD-LEDs. In contrast to previously reported high-efficiency QD-LEDs that use spin-casting to deposit multiple QD layers to achieve saturated QD-LED emission,20–22 our method allows us to minimize the use of QDs (reducing the cost of fabrication and operating device voltage) while maintaining QD-LED EL color purity. The demonstrated large color gamut from QD-LEDs exceeds the performance of both LCD and organic LED (OLED) technologies, suggesting future use of QD-LEDs in high definition, accurate color flat panel displays and in general lighting sources.5

The present work demonstrated a contact printing method for depositing patterned QD monolayer films that are formed by spin-casting QDs onto chemically functionalized PDMS stamps. The method enables insertion of QD monolayers into arbitrary thin film device structures without exposing the constituent thin films to solvents or resorting to phase
separation methods to form QD layers. Inherent to this printing method is the ability to form patterned QD monolayer features, which in this work we used to demonstrate multicolor QD-LED structures with electroluminescent area resolution of $25\,\mu m$. (See the Supporting Information for the demonstration of additional QD film features as small as $150\,nm$.) The demonstrated printing technique now enables formation of arbitrarily complex multilayer structures containing QDs, which can elucidate the physical operating mechanisms that govern operation of QD optoelectronics and lead to design of QD-containing structures of superior performance.\textsuperscript{19}

**Materials and Methods.** We prepare PDMS elastomer stamps by mixing PDMS base with a curing agent (Dow Corning Sylgard 184 silicone elastomer) at the ratio of 10:2. The mixture is then poured into a Petri dish that may contain silicon masters with relief patterns if patterned films are desired. The dish is then placed under low vacuum at room temperature to eliminate air pockets generated by the mixing process. After air pockets have collapsed, the mixture is brought to atmospheric pressure and cured at room temperature for $\sim 7$ to 10 days. The curing process can be accelerated by baking the mixture at $60\,^\circ C$ for $\sim 5$ h. The cured PDMS block is then released from the Petri dish and silicon masters and cut into $\sim 1\,cm^3$ cubes.

We use CVD to deposit between 150 and 200 nm thick layers of parylene-C onto PDMS stamps; the CVD precursor (dimer, $n = 2$ in the chemical structure shown in the inset of Figure 2) is purchased from PARA TECH Coating, Inc.

Colloidal QDs are synthesized and purified according to the procedures reported in ref 15 (for red CdSe/ZnS core shell QDs), ref 17 (for green ZnSe/CdSe/ZnS core−double shell QDs), and ref 18 (for blue CdS/ZnS core−shell QDs).

During QD-LED fabrication PEDOT:PSS (H.C. Starck, Inc.) is deposited via spin-casting onto ITO-coated glass (Thin Film Devices, Inc.) The organic charge transport layers (TPD, CBP, TAZ and Alq3 purchased from H. W. Sands Corp.) and Ag/Mg cathode are deposited by physical vapor deposition at pressures $\leq 10^{-6}$ Torr and evaporation rates $\leq 0.2\,nm/s$.

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**Supporting Information Available:** Description of patterning QD films by molding, calibrating QD solutions by AFM, plots of the electroluminescence spectra of patterned QD-LEDs of Figure 3d, and electronic characteristics of QD-LEDs employing CBP as a hole-transporting layer. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 4.** (a) Electroluminescent red, green, and blue QD-LED pixels with the device structure shown in (b). (b) Schematic diagram shows the cross section of an archetypical QD-LED. (c) A high-resolution AFM micrograph shows a close-packed monolayer of QDs deposited on top of the CBP hole transporting layer prior to deposition of hole blocking and electron transporting layers. Here unpatterned elastomer stamps are used to produce continuous QD monolayers. (d) Chromaticity diagram shows the positions of red, green, and blue QD-LED colors, an HDTV color triangle is shown for comparison. (e) Normalized EL spectra of fabricated QD-LEDs corresponding to the CIE coordinates in (d). QD-LED images and EL spectra are taken at video brightness (100 cd/m$^2$), which corresponds to the applied current density of 10 mA/cm$^2$ for red QD-LEDs, 20 mA/cm$^2$ for green QD-LEDs, and 100 mA/cm$^2$ for blue QD-LEDs.
References
(7) As a part of the development process of our contact printing technique, we employed this procedure in fabrication of QD-LEDs reported in ref 6. Although, not explicitly stated in ref 6 all QD-LEDs described in that letter contain printed QD monolayers.

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