

## **Organic and Nanostructured Materials in Optoelectronic Applications: Physical Processes and Active Devices**

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### **Introduction**

Our research is focused on deciphering the physical properties that govern behavior of nanostructured materials and applying the findings to development of practical, active technologies. With focus on organic and inorganic-nanocrystal electronic and optoelectronic structures, to date we demonstrated efficient LEDs, lasers, solar cells, photodetectors, transistors, memory cells, and chemical sensors. In addition to working on small-molecular-weight van-der-Waals-bonded organic thin films, we also examine hybrid organic/inorganic structures, polymer solids, and self-assembled materials. Our work tends towards the nano-scale where through development of new patterning and materials growth techniques we aim to reduce the size of active device layers from the present nano-scale thickness of organic thin films to that of single molecules or atomic clusters. Our ultimate goal is to utilize the nano-scale functionality of molecules, polymers, and inorganic/organic hybrid assemblies in practical nano-scale devices and both small- and large-area integrated systems.

## 1. Strong Coupling of Light and Matter in a Microcavity LED

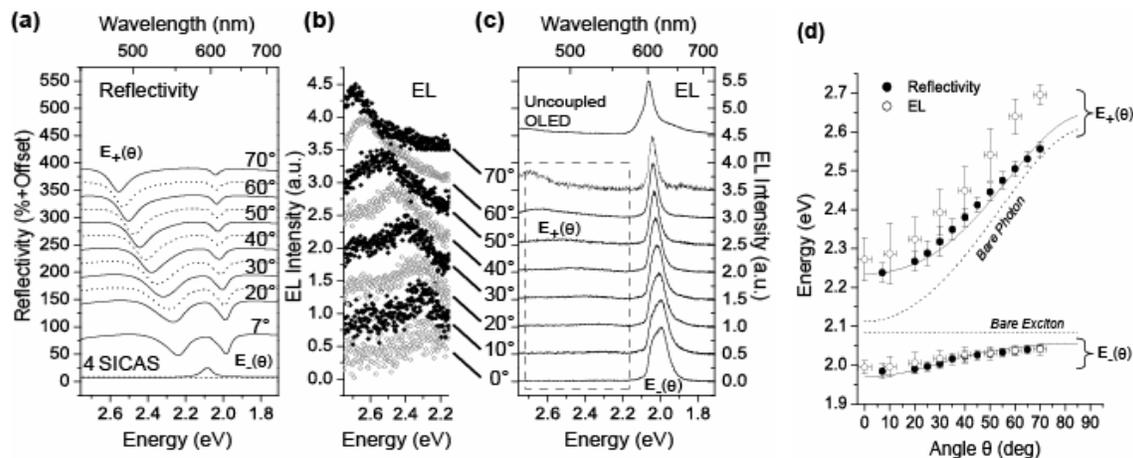
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DARPA Optocenter, NDSEG, NSF-MRSEC

### Project Staff

J.R. Tischler, M.S. Bradley, V. Bulović

We have demonstrated the first microcavity light emitting device (LED) in which light emission is produced from strongly coupled states of light and matter by electrical excitation [1]. Applications of strong coupling in atomic and semiconductor systems have led to one-atom zero threshold lasers, high gain polariton parametric amplifiers, and predictions that strong coupling may play a key role in future quantum information processors. These previous experiments have all relied on optical pumping. We achieve strong coupling in the microcavity LED by electrically exciting a  $6\pm 1$  nm thick film of J-aggregated dye which we embedded into a resonant cavity organic LED (RC-OLED) structure. Specifically, the film of J-aggregated dye is comprised of the anionic cyanine dye TDBC which is electrostatically adsorbed to the cationic polyelectrolyte PDAC (poly diallyldimethylammonium chloride). These films contain a high density of J-aggregated TDBC and therefore have very large peak absorption constant ( $\alpha \sim 1.0 \times 10^6 \text{ cm}^{-1}$ ). We achieved a coupling strength (Rabi-splitting) of  $\hbar\Omega = 265 \pm 15 \text{ meV}$  with 6 nm thick films of active material and even larger coupling strengths should be achievable with thicker films. Figure 1 shows that the device exhibits angular dispersion in the reflectivity and electroluminescence measurements that is characteristic of the strong coupling limit.



**Figure 1** Angularly resolved polariton electroluminescence, reflectivity and dispersion relations for near resonantly tuned polariton RC-OLED. (a) TE polarized reflectivity. Data of successive measurements are offset by 50 percentage points. The reflectivity at  $\theta = 7^\circ$  of a 6 nm thick PDAC/TDBC film (4 SICAS), is shown for comparison. (b) Expanded view of higher energy portion of the EL spectra, normalized to emission of the higher energy polariton peak,  $E_+(\theta)$ , in the  $\lambda = 450 \text{ nm}$  to  $\lambda = 575 \text{ nm}$  range. (c) EL spectra normalized to lower energy polariton peak,  $E_-(\theta)$ . The EL spectrum at  $\theta = 0^\circ$  of an uncoupled OLED is shown for comparison. (d) Polariton angular dispersion relation for RC-OLED of parts (a-c) with  $E_{ph}(\theta = 0^\circ) = 2.11 \text{ eV}$ . The fit is generated from reflectivity data in (a) using the two-state model of Eq. 1, with the coupling interaction,  $\hbar\Omega = 265 \text{ meV}$ .

### REFERENCE

- [1] Tischler, J.R., M.S. Bradley, V. Bulovic, J.H. Song, A. Nurmikko, "Strong Coupling in a Microcavity LED", *Phys. Rev. Lett.* (2005).

## 2. Microcontact Printing of J-Aggregate Thin Films for Photonic Devices

### Sponsors

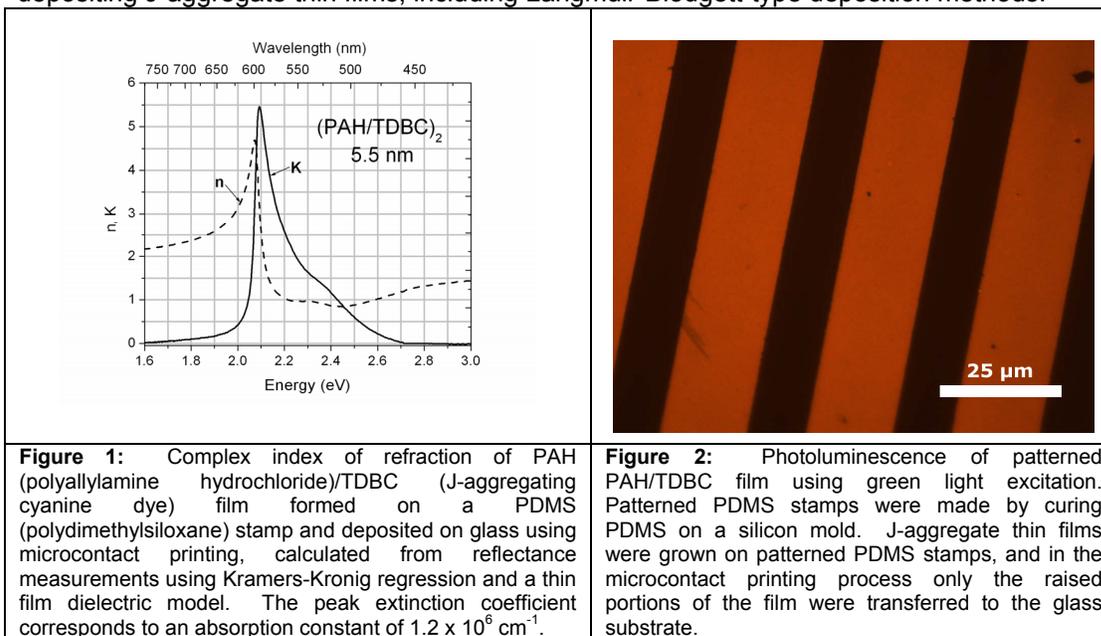
DARPA, NDSEG, MIT NSF MRSEC

### Project Stadd

M.S. Bradley, J.R. Tischler, V. Bulović

Thin film J-aggregates of cyanine dyes enable the observation of strong coupling between light and matter at room temperature, potentially allowing for the development of an entirely new class of optoelectronic devices [1]. Previously, J-aggregate deposition methods have required the exposure of a device in fabrication to the solvents of a J-aggregate solution which can potentially damage other optically or electrically active materials and restrict the process steps involved in fabricating devices. In this work, we demonstrate a new stamping technique for depositing J-aggregate thin films that decouples the formation of J-aggregates from the placement of J-aggregate thin films into device structures.

Combining research in polyelectrolyte layer-by-layer deposition of J-aggregates [2] with stamping of polyelectrolyte thin films, we show how to form thin films of J-aggregates on a stamp and then stamp those films into device structures [3]. We show the optical and morphological properties of stamped J-aggregate films and calculate the optical constants of the films (Figure 1), which we use to determine the density of J-aggregated dye molecules in the final thin film. Additionally, we investigate device structures enabled by stamping of J-aggregate thin films, including J-aggregate organic light-emitting devices and patterned J-aggregate devices made via stamp pattern transfer (Figure 2). Lastly, we explore the extension of J-aggregate thin film stamping to other methods of depositing J-aggregate thin films, including Langmuir-Blodgett-type deposition methods.



**Figure 1:** Complex index of refraction of PAH (polyallylamine hydrochloride)/TDBC (J-aggregating cyanine dye) film formed on a PDMS (polydimethylsiloxane) stamp and deposited on glass using microcontact printing, calculated from reflectance measurements using Kramers-Kronig regression and a thin film dielectric model. The peak extinction coefficient corresponds to an absorption constant of  $1.2 \times 10^6 \text{ cm}^{-1}$ .

**Figure 2:** Photoluminescence of patterned PAH/TDBC film using green light excitation. Patterned PDMS stamps were made by curing PDMS on a silicon mold. J-aggregate thin films were grown on patterned PDMS stamps, and in the microcontact printing process only the raised portions of the film were transferred to the glass substrate.

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- [4] M.S. Bradley, J.R. Tischler, S.K. LaiHing, and V. Bulovic, "Deposition of J-Aggregate Thin Films via Stamping for Use in Optoelectronic Devices," presented at the *Materials Research Society Fall 2005*.

### 3. Critically Coupled Resonators in Vertical Geometry, Capable of Absorbing Nearly 100% of Incident Light in a 5 nm Thick Absorber Layer

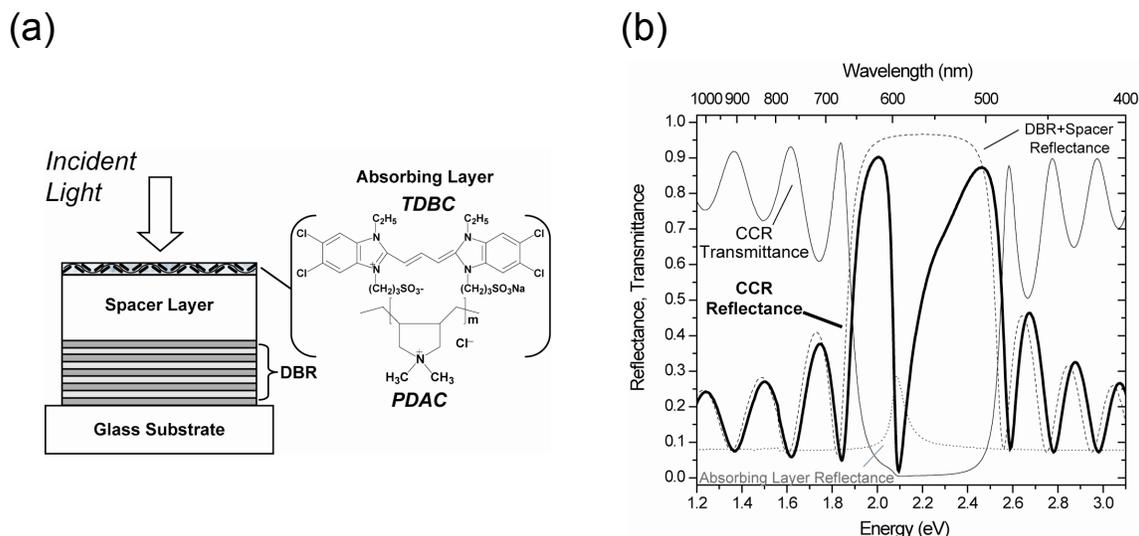
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#### Project Staff

J.R. Tischler, M.S. Bradley, V. Bulović

When light of wavelength  $\lambda_c = 584$  nm is incident on the CCR of Figure 2a from the absorbing layer side of the device, the measured reflectance is  $R = 2\%$ . In contrast, for the DBR with spacer but without the absorbing layer, the reflectivity at  $\lambda_c = 584$  nm exceeds 95%, showing the dramatic change in reflectance due to critical coupling. For the same CCR, the transmittance at  $\lambda_c$  is  $T = 1\%$ . Consequently, 97% of the incident light is absorbed within the  $5.1 \pm 0.5$  nm thick absorber layer, yielding a maximum effective absorption coefficient of  $\alpha_{\text{eff}} = 6.9 \times 10^6 \text{ cm}^{-1}$ . We developed a generalized model of the CCR phenomenon and have shown through simulation that critical coupling is achievable with a variety of material sets, providing several general conditions are satisfied. Among non-epitaxially grown materials, we can envision building CCR's with organic polymers that are used in biological assays and chemical sensors, with molecular materials that are used in photodetectors and xerographic photoresistors, and in the emerging uses of colloiddally grown inorganic nanocrystal quantum dots (QDs). Application of the CCR phenomenon can also facilitate development of single photon optics where it is desirable to absorb a photon with 100% probability in the thinnest possible films and colloiddally grown semiconductor saturable absorber mirrors (SESAMS) for ultra-fast optical modulators.



**Figure 2** (a) Critically coupled resonator (CCR) structure. The device consists of a dielectric Bragg reflector (DBR), a transparent spacer layer, and a layer of J-aggregate cyanine dye. The J-aggregate layer consists of the cationic polyelectrolyte, PDAC, and the anionic cyanine dye, TDBC. Reflection and transmission measurements are made with light incident from the J-aggregate side of the device. (b) Reflectance and transmittance data for the neat PDAC/TDBC film and for the dielectric stack consisting of DBR with spacer layer. At  $\lambda_c = 584$  nm, the CCR absorbs 97% of incident light.

#### 4. Charge Dynamics in Organic Heterojunction Lateral Photoconductors

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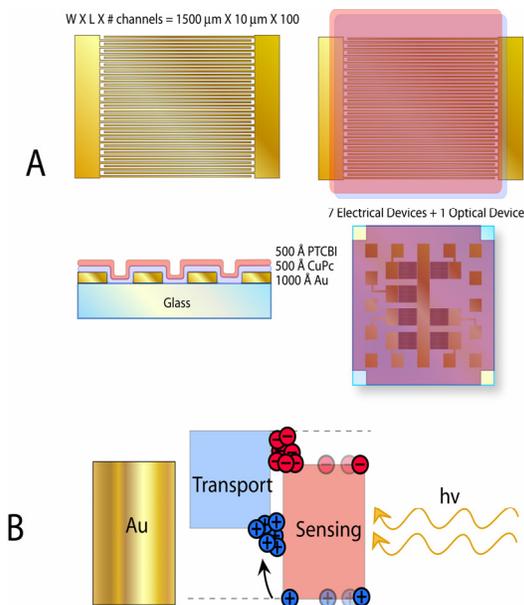
MIT Institute for Soldier Nanotechnologies

##### Project Staff

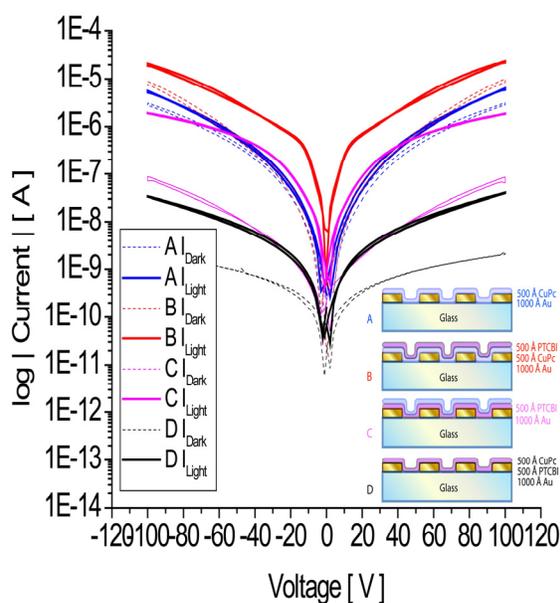
J. Ho and V. Bulović

The purpose of this project is to develop solid-state, organic device structures capable of efficiently converting chemical analyte detection into an electrical signal. The main advantage to using organic materials is that they are synthetically flexible and can be tailored to respond to specific analytes. Our proposed device structure is a heterostructure consisting of an optically active, chemosensing layer and a charge transport layer arranged in a lateral photoconductor-style device (Figure 1A). The advantages to physically separating the sensing and transport functions in chemical sensors are 1) the ability to optimize the transduction of luminescence to device current, and 2) the development of a reusable device platform for a variety of chemosensing applications.

In addition to developing a novel device platform for chemical sensing, we are using this novel structure to study charge transport and exciton dynamics in organic thin films (Figure 1B). The devices consist of a series of gold interdigitated fingers ( $W \times L = 1500\mu\text{m} \times 4\mu\text{m}$ ) spaced  $10\mu\text{m}$  apart (Figure 1A). The gold electrodes are photolithographically defined on glass before the organic layers are thermally evaporated. Locked-in measurements of the photocurrent spectra suggest external quantum efficiencies ranging from 10-15%. Initial experiments indicate an enhancement in photoresponse of the heterostructure devices over devices made from bulk films of both materials (Figure 2).



**Figure 1:** A) Schematic drawings of lateral photoconductor devices. Clockwise from upper left are photolithographically defined gold electrodes, electrodes with evaporated organic thin films, cross-section view, top view of actual substrate. B) Mock band diagram of device showing exciton generation, exciton diffusion, and charge carrier build-up at the heterostructure interface.



**Figure 2:** Semi-log Current-Voltage characteristics of bulk and heterostructure lateral photoconductor devices. Dotted lines represent I-V curves in dark. Solid lines represent I-V curves under LED illumination centered at  $\lambda = 532\text{nm}$ . Inset: Cross-sections of tested devices. Note the different photoresponse curves between the bulk and heterostructure devices.

## 5. Energy Disorder and Device Performance in Organic Electronics

### Project Staff

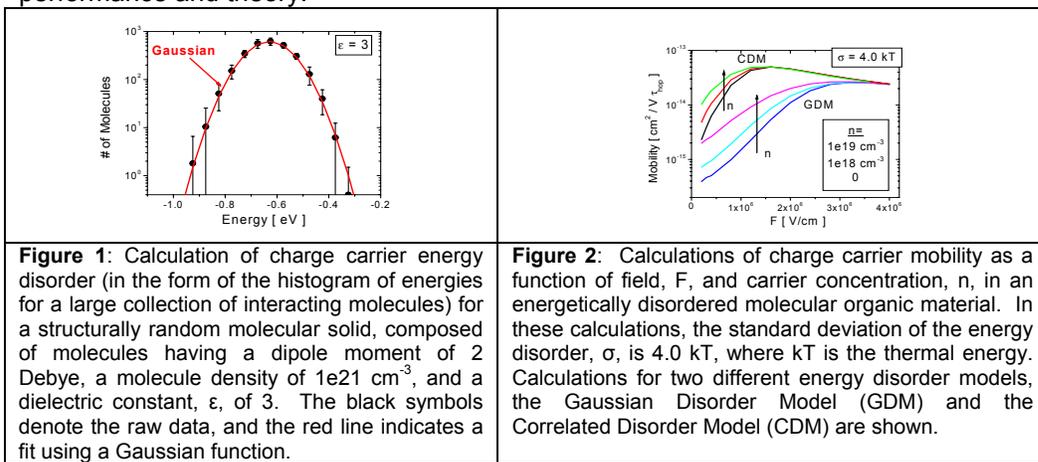
C. F. Madigan and V. Bulović

### Sponsors

MARCO Focused Research Center for Materials, Structures, and Devices (MSD), NDSEG Fellowship

Presently many organic electronic devices employ amorphous materials, and it is well known that the molecular energy levels in such materials are subject to disorder arising from variations in local intermolecular interactions. The performance of such devices is largely controlled by the movement of molecular charge carriers and excitons through the constituent materials, and it has been well established that energy disorder strongly influences charge carrier and exciton motion. Though accurate analytic treatments remain elusive, Monte Carlo (MC) simulations of charge carrier and exciton hopping between molecular sites subject to energy disorder have proven an effective tool for analyzing charge carrier and exciton motion in such materials [1]. By combining MC simulations with accurate models of energy disorder, it should be possible to perform calculations of real device behavior with relatively few model assumptions.

In this project two problems are addressed: (1) the theoretical calculation of energy disorder in amorphous organic materials; and (2) the application of MC simulations to realistic device structures and operating conditions. We have performed exact calculations of charge carrier and exciton energy disorder arising from electrostatic interactions between structurally disordered, polarizable molecular charge distributions (see Figure 1). These calculations differ from those in the literature because the molecular polarizability is explicitly included in the calculation, avoiding the need for dielectric continuum approximations (DCAs). It is found that the widely employed DCAs are inaccurate, and we are presently developing improved expressions for relating the magnitude of the disorder to the material properties (principally, the molecular dipole moment, the energy state density, and the dielectric constant). We have also developed a MC simulator of charge carrier and exciton motion in energetically disordered molecular materials capable of treating realistic device geometries (e.g. multilayer stacks, electrical contacts). Because organic electronic devices often operate at high carrier concentrations, we have also included basic charge carrier interactions to treat carrier concentration effects on charge transport, which have not been previously investigated using the MC simulation technique. We are presently performing calculations of carrier mobilities as a function of field and carrier concentration (see Figure 2) for comparison with existing approximate analytic approaches. These studies lead to future simulations of real device structures for a rigorous comparison of experimental device performance and theory.



REFERENCE

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**6. White Light QD-LEDs**

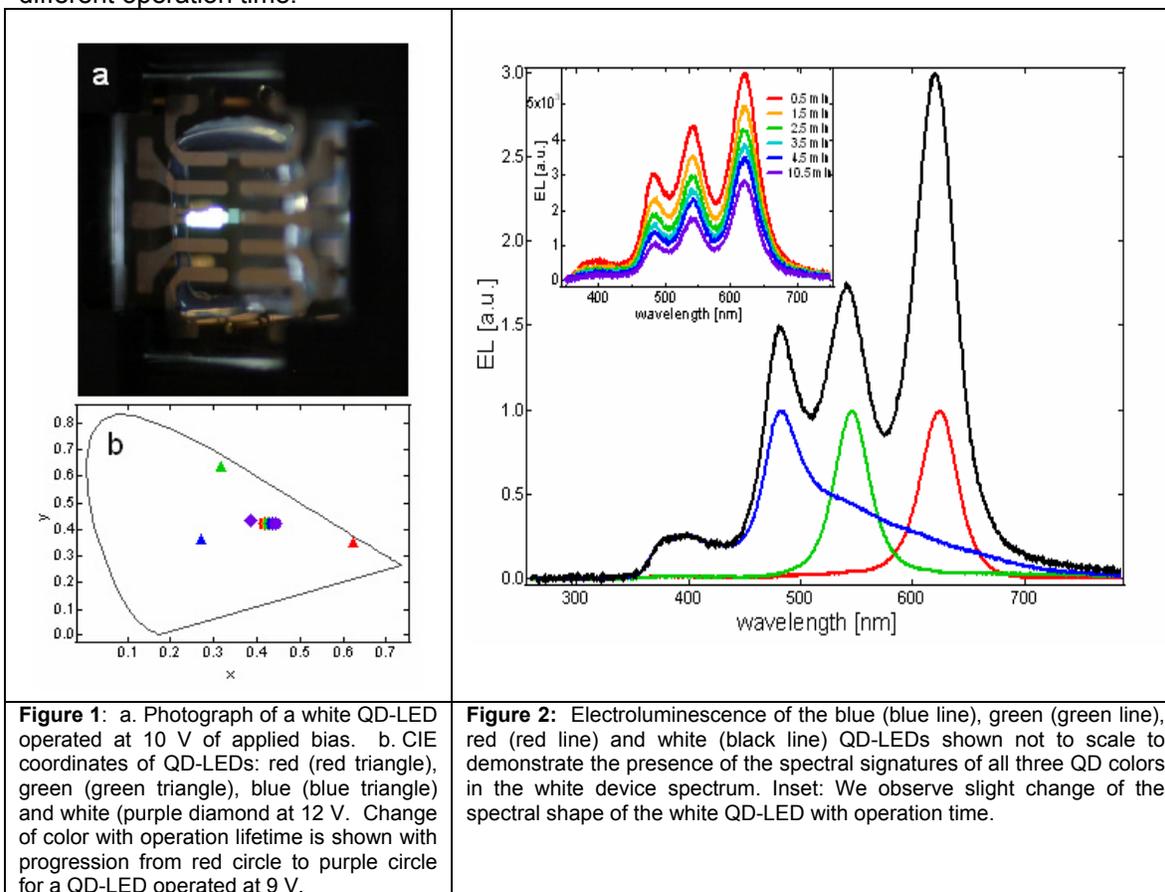
**Sponsors**

MIT Institute for Soldier Nanotechnologies, NSF Materials Research Science and Engineering Center at MIT, Presidential Early Career Award for Scientists and Engineers

**Project Staff**

P. O. Anikeeva, J. E. Halpert, M. G. Bawendi, V. Bulović

We are developing white-light emitting quantum dot LEDs (QD-LEDs) for use as planar white-light sources in the full-color active matrix displays with color filters, and in future solid state lighting. Our white QD-LEDs consist of organic charge transport layers with a QD monolayer sandwiched between them. This device architecture enables independent processing of the charge transport layers and the emissive layer. The independent processing of QDs is a result of the recent development of the QD printing technique, which allows for the solvent-free deposition of QD monolayers onto various organic materials. By mixing different amounts of high quantum yield colloidal core/shell QDs (red CdSe/ZnS, green ZnCdSe/ZnS, blue CdS/ZnS) we demonstrate different QD-LED colors. Figure 1a shows electroluminescence of the white QD-LED with the CIE (Commission International de l'Eclairage) coordinates of (0.42, 0.41). Figure 1b and Inset of Figure 2 also show that CIE coordinates vary only slightly under the different applied bias and different operation time.



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[2] P. O. Anikeeva, J. E. Halpert, M. G. Bawendi, V. Bulović, unpublished results.

## 7. Packing of Quantum Dot Monolayers

### Sponsors

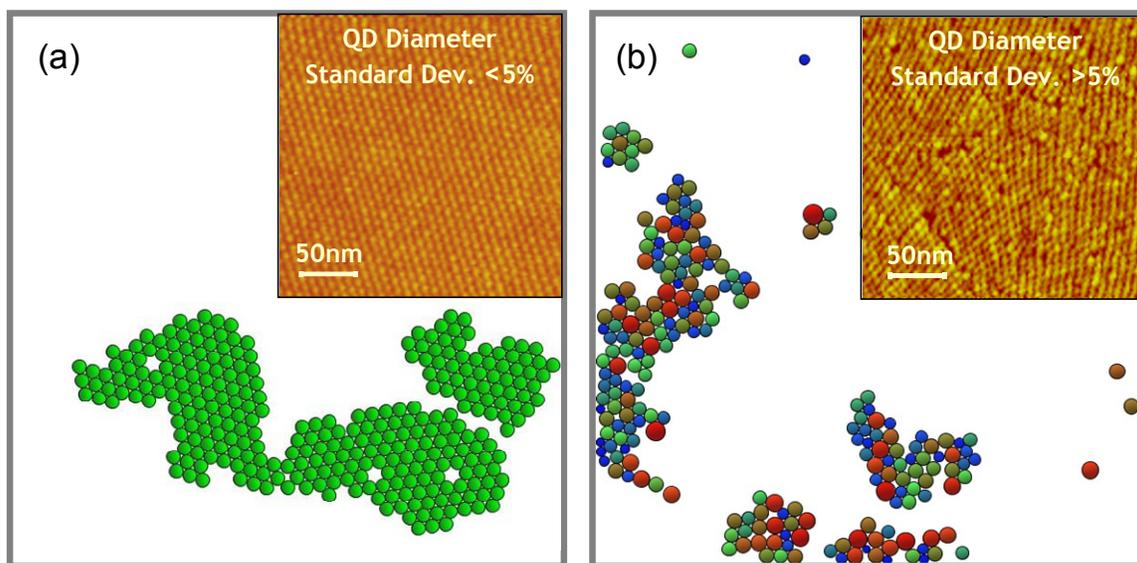
MARCO Materials, Structures, and Devices (MSD) Center

### Project Staff

Ethan Howe and Vladimir Bulović

We developed a kinetic model for assembly of ordered quantum dot (QD) monolayers on 2-dimensional surface that reproduces experimental observations for a variety of QD size distributions (of Gaussian size profile). Such QD monolayers have already been utilized in a number of thin-film applications, QD-LEDs and QD-photodetectors. However, methods of fabrication of QD films are still being developed and our work focuses on developing a numerical tool to investigate methods for improving the quality of these films.

To numerically assemble a QD monolayer, we model the QDs as spheres that moves on the surface with no friction but with random thermal motion added at each time step. We apply a van der Waals attraction between QDs and hard-wall repulsion at the QD radius. When two QDs collide, their interaction is partially inelastic based on a model parameter. These conditions allow for a range of behavior encompassing many interesting phenomena. We find that a mono-disperse size distribution of QDs forms hexagonally close-packed aggregates, and the packing and aggregate stability of the QD monolayer degrades dramatically as the standard deviation of the size distribution is increased. In experimental studies [1], the instability of QD monolayers has been observed to occur for standard deviations of greater than 10% in QD diameter. We were able to reproduce these findings in our simulations (Figure 1). We have further shown that confining the same QD distributions inside of a 1-dimensional hard boundary with a width of a few QD diameters can counteract this instability.



**Figure 1:** a) Results of simulation of packing for 300 QDs of equal size. The inset is an AFM image [1] of a monolayer of QDs with less than 5% standard deviation in diameters. In our simulation we observe the same hexagonal close-packed arrangement of QDs and stability of aggregates that allows for good monolayer formation. b) Results of simulation for packing 300 QDs with a 15% standard deviation in diameters. The inset is an AFM image for the same method of preparation as a) but with QDs having a greater than 5% standard deviation in diameters. For these large size distributions our simulated dots could no longer form hexagonally close-packed arrays. In addition, aggregates readily broke up as dots were less well-bound.

REFERENCE

[1] S. Coe-Sullivan *et al.*, *Advanced Functional Materials* **15**, 1117-1124 (2005).

**8. Resonant Cavity Quantum Dot LEDs**

**Sponsors**

NSF, Presidential Early Career Award for Scientists and Engineers (PECASE)

**Project Staff**

V. Wood, J.R. Tischler, V. Bulović

Quantum dot LEDs (QD-LEDs), which capitalize on the excellent color saturation and high photoluminescence efficiencies offered by quantum dots, promise to be part of future generation display technologies [1]. The goal of our project is to integrate the already developed technology of the QD-LED into a resonant cavity (RC) and thereby achieve enhanced, directed electroluminescence (EL) that can be of use in fields as diverse as optical communications, spectroscopy, and environmental and industrial sensing.

The RC structure we are currently investigating (Figure 1) consists of a standard QD-LED [1] grown on top of a distributed Bragg reflector (DBR). A DBR is a highly reflective mirror made of  $\lambda/4$  layers of alternating high and low indices of refraction. With a reflectivity of more than 98% in the wavelength region of interest, the DBR serves as one of the cavity mirrors. The other cavity mirror is the Ag doped Mg electrode of the QD-LED.

With this structure, we have achieved narrowed emission, which is evident when comparing EL spectra and images of the QD-LED and the RC QD-LED (Figure 2). The QD-LED appears orange because our eyes sense the red light of the QDs as well as the shorter wavelength emission from the organics. In contrast, the RC QD-LED exhibits effectively monochromatic red light. The plot of peak emission intensity at different angles (Figure 2) shows an emission cone of less than twenty degrees. If the path-length of the cavity does not match the QD emission wavelength, EL from the RC QD-LED is off-normal. We are currently working to understand the emission enhancement capability of our RC QD-LED.

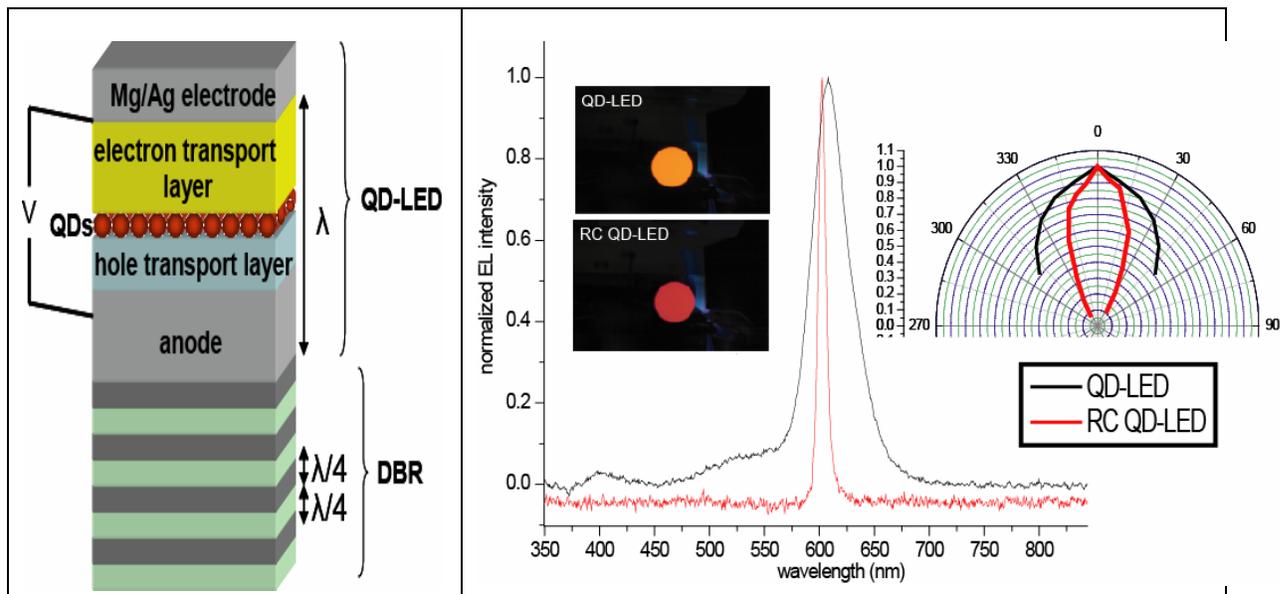


Figure 1: Schematic of RC QD-LED

Figure 2: Comparison of EL spectra, images, and angular emission profiles of RC QD-LED and QD-LED. RC QD-LED exhibits marked narrowing.

REFERENCE

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**9. Quantum Dot Photodetectors Deposited via Microcontact Printing**

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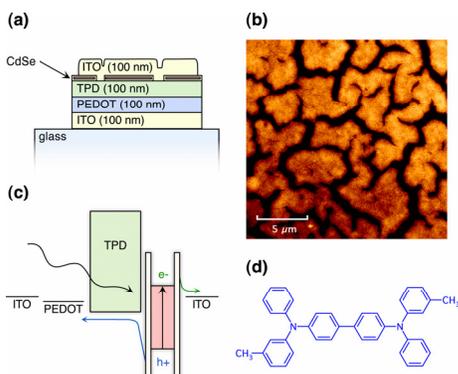
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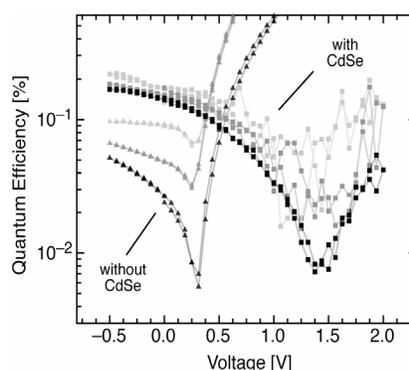
A. C. Arango, D. C. Oertel, M. G. Bawendi, V. Bulović

Solution processable colloidal quantum dot systems exhibit many of the special optical and electronic properties associated with epitaxially grown quantum confined systems. Their tunable band gap and higher absorption relative to the bulk make quantum dots particularly attractive as photogeneration materials. At the same time, colloidal quantum dots offer greater material system flexibility than epitaxial quantum dots because deposition on any substrate is possible. The prevailing deposition method, however, is spin casting [1], which introduces limitations such as solvent incompatibility with underlying films and the inability to pattern side by side pixels for multispectral photodetector arrays. We employ a non-destructive microcontact printing method which allows for deposition of a thin (20 nm) quantum dot film onto a wide band gap organic hole transport layer, N,N'-bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (TPD), thus producing an inorganic/organic heterojunction which serves to enhance charge separation in the device. The top and bottom contacts are provided by ITO electrodes, allowing for near transparency.

Current-voltage characteristics show low dark currents in reverse bias and good rectification. Excitation of the quantum dots yields a strong, saturated photoresponse, open circuit voltages of +0.5V and a fill factor of 0.4. Measurement of the locked-in photocurrent under bias reveals a strong photocurrent signal extending out to +1.5V (Figure 2), in excess of the built-in acceptor-donor energy level offset of ~0.8V. We attribute the photocurrent voltage dependence to efficient charge extraction, low recombination rates at the heterojunction and top ITO contact. By changing the size and material properties of the quantum dots, the response spectrum of the device can be tuned across visible and near infra-red spectrum. The present focus is on improving the device performance and optimizing the photodetection response in the 1um to 2um wavelength region by using different quantum dot film chemistries.



**Figure 1:** Schematic of photodetector device structure (a). An AFM of the surface of the printed quantum dot film demonstrates that the film is not continuous (b). The energy band diagram (c) illustrates the photogeneration process. The molecule structure of the hole transport materials, TPD, is shown in (d).



**Figure 2:** Plot of the quantum efficiency versus applied bias for the photodetector and a control device without quantum dots. The CdSe device is measured with a 532 nm laser at 2, 20 and 200 uW/cm<sup>2</sup> (light grey, grey, and black squares, respectively). The TPD control device is measured at 408 nm at 2, 20 and 200 uW/cm<sup>2</sup> (light grey, grey, and black triangles, respectively)

REFERENCE

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**10. Energy Transfer from an Organic Phosphorescent Thin Film to a Monolayer of Quantum Dots**

**Sponsors**

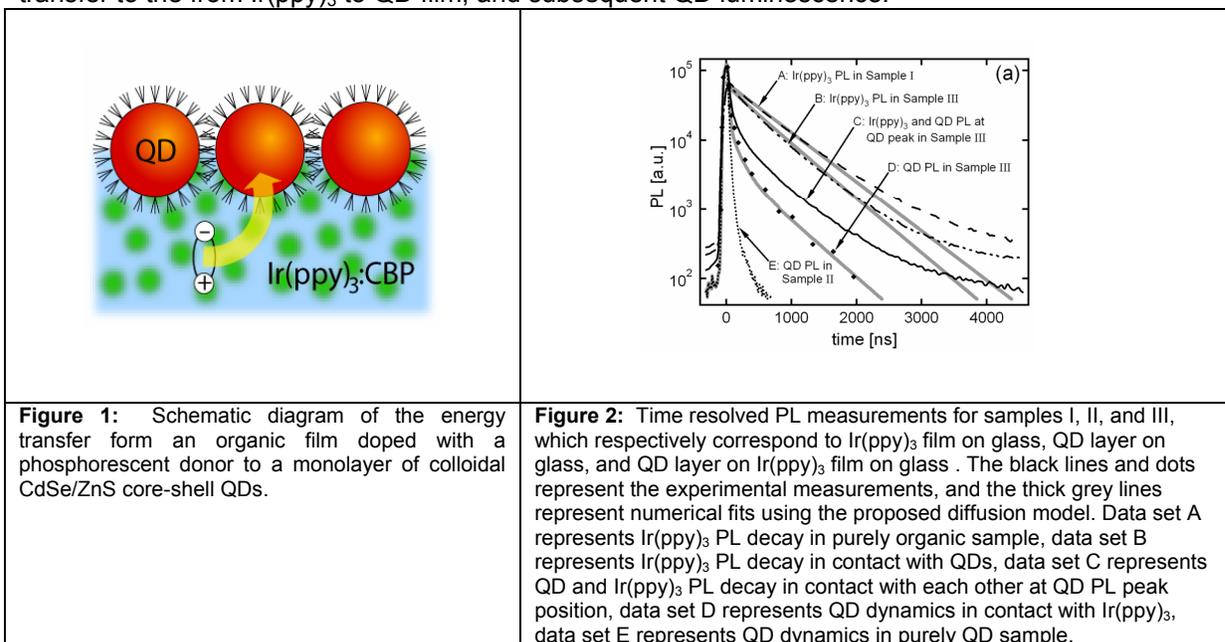
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**Project Staff**

P. O. Anikeeva, C. F. Madigan, S. A. Coe-Sullivan, J. S. Steckel, M.G. Bawendi, V. Bulović

Over the past several years the optical and electronic properties of colloidal synthesized nanocrystals, or quantum dots (QDs), of CdSe have been extensively studied, with the aim of using QD films in solid state opto-electronic devices. Efficient exciton generation in CdSe QDs suggests use of nanocrystal composite films in photovoltaic cells, while high luminescence quantum yields and tunability of QD emission wavelengths over the entire visible spectrum suggests QD film use in light emitting devices (LEDs). These developments are a consequence of advances in colloidal QD synthesis that allow for increased control over the shape, size, and emission wavelength of nanocrystals, and the development of methods for forming QD thin films of controlled structure and composition. We utilize these advances in the present study to demonstrate triplet exciton energy transfer (ET) from a thin film of phosphorescent molecules to a monolayer of CdSe/ZnS core/shell QDs (see Fig. 1). Triplet exciton harvesting and transfer to an efficient lumophore has been previously used in advancing organic light emitting device (OLED) technology, and has the potential to similarly benefit the emerging field of quantum-dot-LEDs.

The efficient energy transfer is facilitated by the spectral overlap of the organic phosphor fac tris(2-phenylpyridine) iridium ( $\text{Ir}(\text{ppy})_3$ ) luminescence and QD absorption spectra. In time-resolved photoluminescence (PL) measurements the energy transfer is manifested as elongation of the QD PL time constant from 40 ns to 400 ns (see Fig. 2), and a concomitant 55 % increase of time-integrated QD PL intensity. Numerical analysis supports the conclusion that the observed PL dynamics are dominated by exciton diffusion within the  $\text{Ir}(\text{ppy})_3$  film to the QD layer, energy transfer to the from  $\text{Ir}(\text{ppy})_3$  to QD film, and subsequent QD luminescence.



REFERENCE

[1] P. O. Anikeeva, C. F. Madigan, S. A. Coe-Sullivan, J. S. Steckel, M.G. Bawendi, V. Bulović, *Chemical Physics Letters* (2006).

11. Optical-Feedback OLED Display Using Integrated Organic Technology

Sponsorship

MARCO Focus C2S2, MARCO MSD

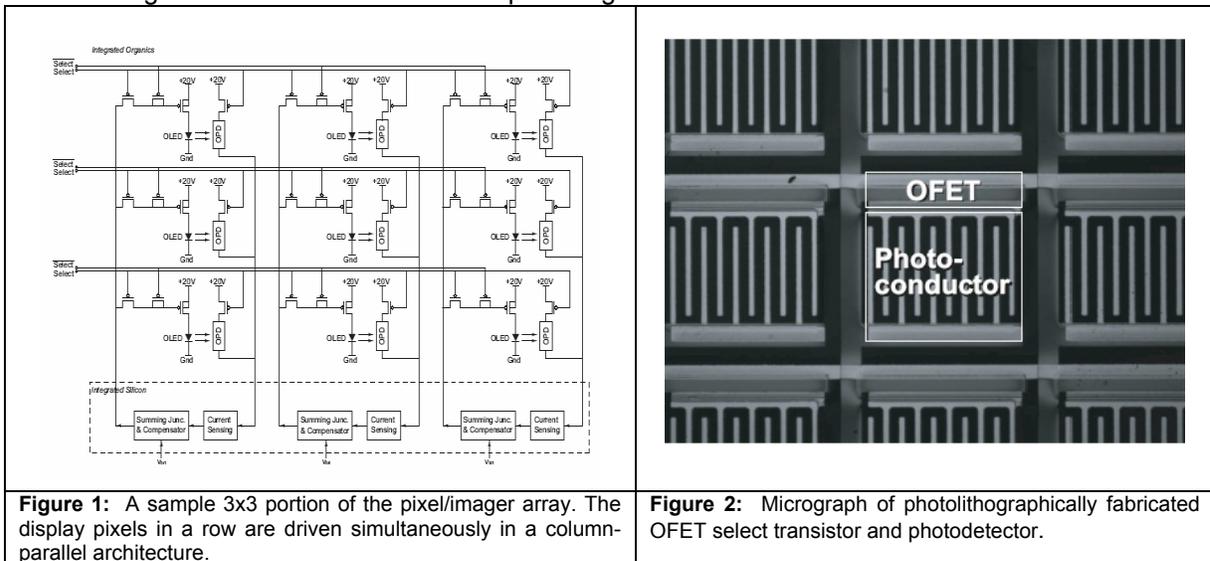
Project Staff

Nausieda, I. Kymissis, V. Bulović, C. G. Sodini

Organic light emitting diodes (OLEDs) are a promising technology for large, thin, flexible displays. OLEDs are emissive, thereby removing the need for a backlight and decreasing display thickness. Compared to typical light-valve displays, OLEDs exhibit improved contrast ratio, faster response times, and a larger color gamut. However, OLEDs possess non-linear light output characteristics, and their power efficiency drifts over time due to operational degradation. This degradation produces pixel to pixel variation in output characteristics, as well as decreasing the display's overall lifetime. We propose to drive OLEDs to the desired brightness using optical feedback on the pixel level. Preliminary research[1] has shown that feedback will improve the display lifetime by six to tenfold. This project aims to build a complete system that encompasses the design and fabrication of an integrated silicon control chip and an organic pixel/imaging array, which will together form a stable, usable display.

The integrated silicon control chip is composed of multiple channels which each contain two main blocks: the current sensing block and the feedback compensation block (Figure 1). The former is a transimpedance amplifier that converts the organic photodetector output current to a voltage. The feedback compensation block stabilizes the loop, ensuring a desirable response time and phase margin, and is implemented using a National Semiconductor .35µm process.

The organic pixel/imager array consists of organic field effect transistors (OFETs) that select and control OLED pixels and photodetectors. The OFET and photoconductor electrode arrays are fabricated using a photolithographic process[2] (Figure 2). Currently, a technique to thermal ink-jet print the organic photoconductor to save photolithographic steps is being explored. We acknowledge National Semiconductor for providing the fabrication services.



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**12. Amorphous zinc-oxide-based thin film transistors**

**Sponsors**

Hewlett-Packard Company

**Project Staff**

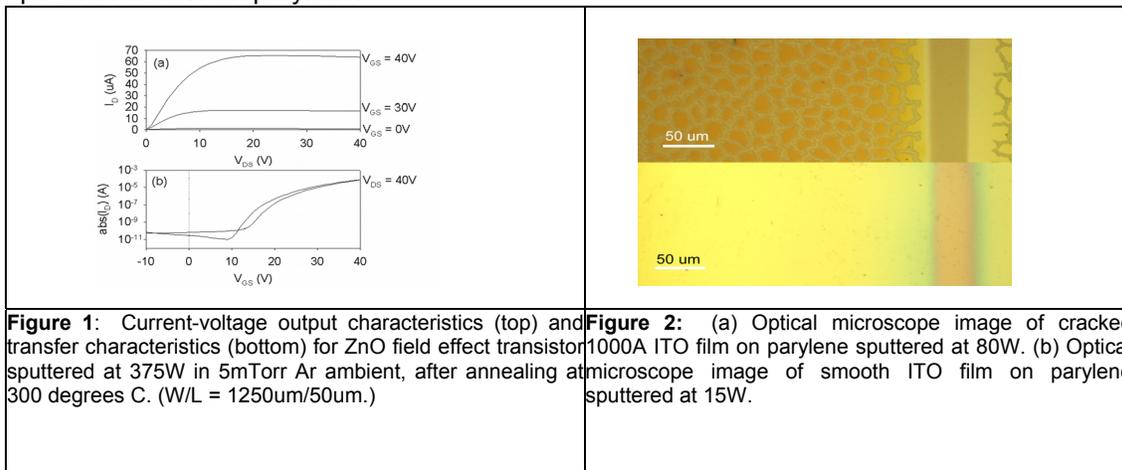
A. Wang, I. Kymissis, V. Bulović, C. Sodini and A. I. Akinwande

RF-sputtered zinc oxide-based field effect transistors (FETs) have been demonstrated recently with higher mobilities and performance than amorphous silicon, the dominant material used for display backplanes [1,2]. The low temperature processing possible for zinc oxide-based FETs [3] makes these materials compatible with flexible polymer substrates, but patterning with shadow masks limits feature size and accuracy. This project aims to develop a low-temperature, lithographic process for zinc oxide-based FETs, similar to one developed for organic FETs [4].

Our initial work focuses on two issues: determining optimal conditions for (1) growing the oxide semiconductor and (2) depositing high quality oxide semiconductor and contact films on an organic polymer, parylene.

For (1), top-contact, bottom gate ZnO FETs were fabricated on Si/SiO<sub>2</sub> substrates, using SiO<sub>2</sub> as the gate dielectric and Si as the gate, and sputtered indium-tin-oxide (ITO) as source/drain contacts. The RF sputtering power, total chamber pressure, and annealing temperatures were varied in a series of experiments, and Fig. 1 shows the current-voltage characteristics of a device from one set of conditions.

For (2), ITO films were deposited on an organic polymer dielectric, parylene, at different sputter rates. High stress in the oxide films on top of the soft organic polymer dielectric, parylene, may cause cracking and discontinuities in the film. Fig. 2a shows a microscope photograph of the cracked surface of an ITO film sputtered at 80W on parylene; Fig. 2b shows a continuous ITO film sputtered at 15W on parylene.



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### 13. Patterning Micron-Sized Features of Quantum Dots and Metal Electrodes

#### Sponsors

MIT Institute for Soldier Nanotechnologies, NSF Materials Research Science and Engineering Center at MIT, Presidential Early Career Award for Scientists and Engineers

#### Project Staff

J. Yu, J. Chen and V. Bulović

Organic LED (OLED) and quantum dot LEDs (QD-LED) are a promising technology for the emissive element in flat panel displays. However, organic material in these devices are isensitive to solvent exposure and create processing challenges in patterning a pixelated display. This project aims to develop novel fabrication processes for OLED and QD-LED displays.

In QD-LEDs, quantum dots can be patterned by spin-casting a monolayer onto a relief poly(dimethylsiloxane) (PDMS) stamp and then transferring the pattern onto an organic substrate [1]. However, the spin cast process requires significant use of material. An alternative solution is to directly pattern the dots using thermal inkjet pico-fluidic drop dispensing system (TIPS) provided by Hewlett-Packard (Figure 1(a)). A process for formation of patterned monolayer using this technique is currently being developed.

Patterning of electrodes in OLED or QD-LED displays is presently done primarily by shadow masking, which is limited in resolution, or cold-welding which requires high pressures, additional protection layers, use of gold electrode, or subsequent dry etching steps [2,3]. As an alternative, we are investigating subtractive patterning of silver or silver-magnesium electrodes with untreated PDMS stamp. We demonstrated 25  $\mu\text{m}$  feature sizes with good yield on 20nm thick silver-magnesium films (Figure 1(b)). This PDMS lift-off technique applied on an OLED electrode made of 50 nm silver film on top of 50 nm silver-magnesium yields OLEDs with the same quantum efficiency and current voltage characteristics to OLEDs defined by shadow masking (Figure 2).

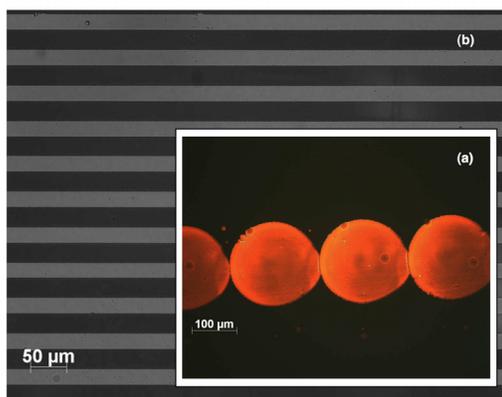


Figure 1

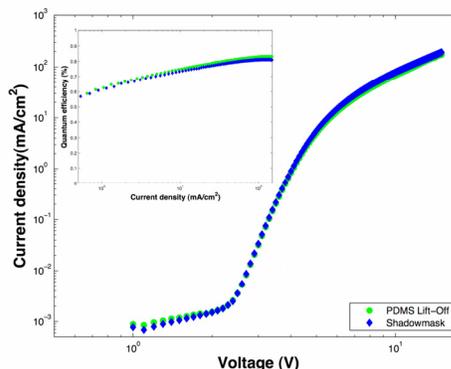


Figure 2

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## 14. Organic Optoelectronic Devices Printed by the Molecular Jet Printer

### Sponsors

Hewlett-Packard Company

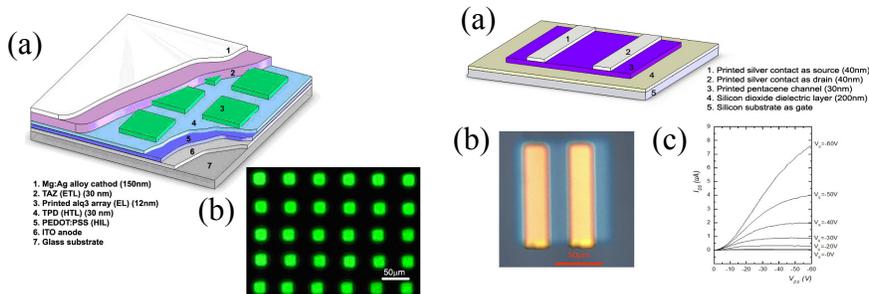
### Personnel

J. Chen, V. Leblanc, M.A. Baldo, M.A. Schmidt and V. Bulović

Using a microfabricated silicon printhead we developed a novel printing technique, molecular jet printing (MoJet) [1,2], that allows direct patterning of small molecular weight organics and metals by additive deposition at high resolution.

Today's dominant method for patterning vacuum deposited semiconducting molecular organics uses a thin metal stencil as a shadow mask through which material is evaporated. Once the metal stencil is fabricated, it cannot be reconfigured to define arbitrary pattern, or be scaled up with substrate size. In contrast, the MoJet printing technique utilizes a silicon printhead that integrates a moving micro-shutter with a micro-aperture. The shutter can be opened or closed with a DC control signal. Evaporated organic molecules can either pass through the aperture to reach the substrate when no bias is applied, or can be obstructed by the shutter when the control signal is above 30V DC. This reconfigurable printhead together with a moving stage allows arbitrary patterning capability and scalability of the MoJet printer to larger substrate sizes.

We demonstrate that active organic devices such as organic LEDs and organic FETs (see graphics below) can be directly fabricated using the MoJet printer. The MoJet printing is a solvent-free process (in contrast to ink-jet printing) and combines the high quality of thermally evaporated thin films with the high precision and scalability enabled by MEMS technology. The MoJet printed organic electronic devices have the same performance characteristics as those defined by shadow mask patterning method, but the size of the substrate plate can now be expanded beyond GEN 2/3. As such, MoJet printer surpasses the capability of metal stencil shadow mask and has the potential to become the next generation patterning tool for making organic optoelectronic devices.



**Figure 1:** (a). Layer structure of printed OLED array. The green electroluminescent layer (EL) layer is directly printed with MoJet printer. (b). EL micrograph of active OLED array at 7.5V applied voltage. The image is taken through a 470 nm low pass filter to reveal that green pixel patterned by MoJet. The pixel size is 30 µm, equivalent to 800 dpi resolution.

**Figure 2:** (a). Structure of the printed Pentacene transistor. Pentacene layer is printed down first, and sequentially silver contacts. (b). Micrograph of a single printed OFET on silicon oxide. (c) The I-V characteristics of one of the transistors. The gate voltage  $V_g$  varied from 0 to -60V in 10V steps.

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Michael Scott Bradley, "Highly Absorptive Thin Films for Integrated Photonic Devices," M.Eng. February 2006 (EECS).

Albert Lin, "A Silicon Current Sensing Amplifier and Organic Imager for an Optical Feedback OLED Display," M.Eng. February 2006 (EECS) (co-supervised with C. Sodini).

Kartik Lamba, "An Integrated Circuit for Feedback Control & Compensation of an Organic LED Display," M.Eng. February 2006 (EECS) (co-supervised with C. Sodini).

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