

Organic and Nanostructured Electronics Laboratory

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1. Patterned Removal of Molecular Organic Films by Diffusion

Sponsors

Center for Excitonics, Clare Boothe Luce Foundation

Project Staff

K. E. Aidala, C. E. Packard, S. Ramanan, V. Bulović

Organic light-emitting diodes (OLEDs) and other optoelectronic applications employ molecular organic solids due to their high luminance, efficiency, and contrast ratio [1], but the shadow-masking technology currently used to pattern pixels at the finest level of feature definition requires thin, delicate masks, which are difficult to scale to large-area substrates [2]. Thin films of a variety of molecular organic materials can be patterned using a microcontact printing-based method in which relief-patterned polydimethylsiloxane (PDMS) stamps remove a controlled thickness of the vapor-deposited material without requiring elevated temperatures or applied pressure [3]. In recent work, we have investigated the mechanism of the previously reported subtractive patterning method. Experiments that vary the length of time the stamp remains in contact with a deposited film reveal the process to be time-dependent. Figure 1 shows the time-dependence measured for five different organic materials: TAZ, TPD, spiro-TPD, TPBi, and Alq₃. Despite the differences in the absolute thickness removed, all the materials display similar behavior with respect to stamp contact time: patterning occurs to greater depths the longer the PDMS remains in contact with the organic film. The large amounts of material removed and the overall time-dependence suggest that the mechanism for the removal is not strictly due to adhesion of the organic to the PDMS stamp. These observations, combined with persistent photoluminescence of used stamps despite exposure to oxygen plasma (Figure 2), show that patterning occurs by diffusion of the organic dye molecules into the PDMS. The diffusive nature of the patterning process additionally makes repeated patterning with a single stamp possible, potentially enabling roll-to-roll or wave printing over large areas.

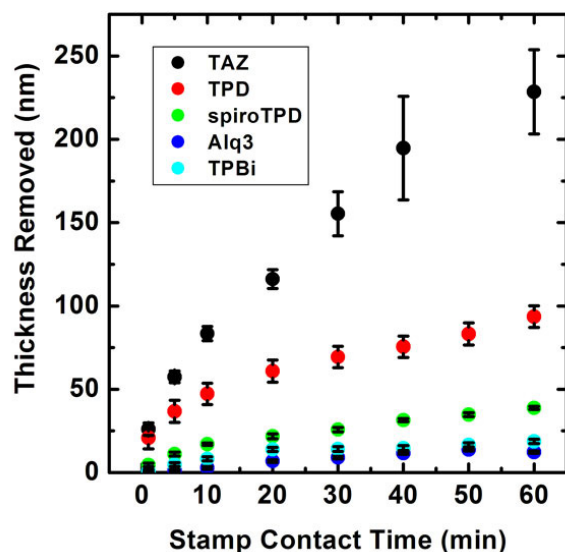


Figure 1: Patterning of molecular organic films shows sensitivity to the time the stamp remains in contact with the film. Patterning through the film thickness can be achieved for combinations of film thickness and contact time that fall below the curves.

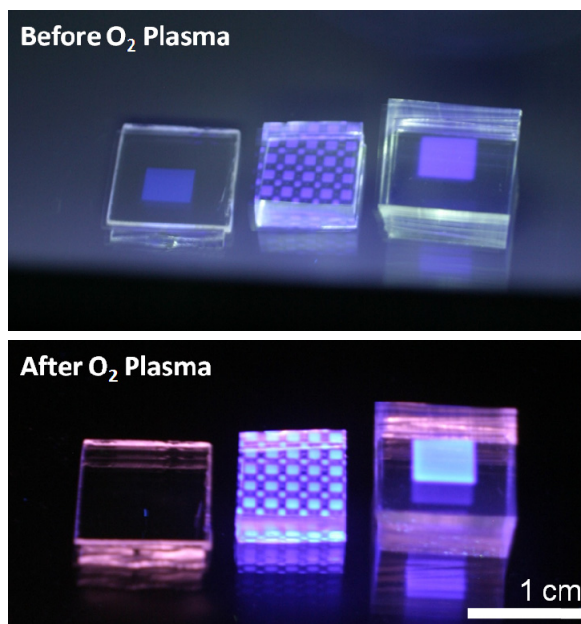


Figure 2: Left to right: 20-nm spiro-TPD evaporated on SiO₂, PDMS stamp used to remove 20-nm spiro-TPD, 20-nm spiro-TPD evaporated on PDMS. After O₂ plasma exposure, the persistence of photoluminescence in PDMS indicates that dye molecules have diffused into the polymer.

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2. Nanoscale Morphology at the Interface Between Colloidal Quantum Dots and Organic Semiconductor Films

Sponsors

Institute for Soldier Nanotechnologies, National Science Foundation

Project Staff

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

The recent development of a hybrid organic/colloidal quantum dot light emitting device (QD-LED) consisting of a single monolayer of quantum dots (QDs) [1] highlights the need to establish rational control of nanoscale morphology, particularly at the interface of two dissimilar materials. The device structure consists of a close-packed monolayer of QDs sandwiched between two organic semiconductor charge-transport layers and carrier-injecting electrodes. The exact positioning of the QD monolayer affects the external quantum efficiency [2, 3]. We examine the degree of interpenetration at the interface between colloidal quantum dots and organic semiconductor molecules commonly employed in QD-LEDs, using tapping-mode atomic force microscopy. We compare different deposition methods, finding the greatest degree of QD penetration for a contact printed (Figure 1) QD layer. The QDs are spun cast onto a parylene coat polydimethylsiloxane (PDMS) "rubber stamp." A substrate already coated with a thin film of or-

organic material is brought into contact with this stamp and subsequently removed. The dots leave the stamp and are embedded in the organic film. We intentionally deposit a sub-monolayer of QDs in order to use tapping-mode atomic force microscopy to image the height at which the QDs emerge from the organic (Figure 2). The height variation of the background organic film is generally greater than the amount that the QD protrudes, requiring a mask to be defined to identify the locations of the QDs. The mask is defined by using the phase image (Figure 2b) from the atomic force microscopy scan, which shows a clear contrast between the QDs and the surrounding organic. After application of this mask to the height image, a histogram of the pixel heights is plotted (Figure 2c). The two roughly Gaussian distributions are easily identified, and the difference in the mean is recorded. The QDs protrude by about 0.7nm in Figure 2, which is a typical value across several different organic materials.

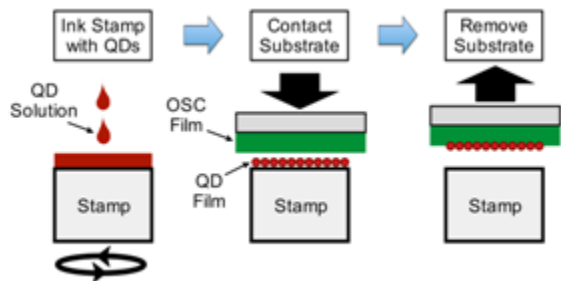


Figure 1: Deposition method for quantum dots (QDs). A solution of QDs is spun-cast onto the stamp. A substrate with an organic film is brought into contact with the stamp and then removed. The QDs are transferred to the organic film.

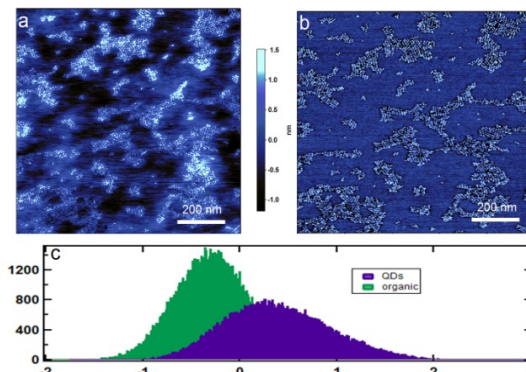


Figure 2: Atomic force microscope data. (a) Topographic image of quantum dots (QDs) in an organic film. (b) Phase image. (c) Histograms of the pixel height of areas containing QDs (blue) and the background organic (green). The difference between the peaks indicates the height at which the dots emerge from the organic.

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3. Ultra-fast Laser Modulation Mediated by Strong Light-matter Coupling

Sponsors

Center for Excitonics, Hertz Foundation, National Science Foundation

Project Staff

G. M. Akselrod, E. R. Young, V. Bulović

Optical computing has the potential to create a paradigm shift in the way information is transmitted and manipulated by creating all-optical data networks and computational circuits with almost unlimited bandwidth and unprecedented energy-efficiency. However, this long-standing dream has thus far been difficult to achieve due to a lack of appropriate material sets, light-matter interactions, and device design necessary to create the optical components that are fast, highly energy-efficient, and capable of being integrated into a larger photonic system. Here we present a micron-scale laser structure with output that is modulated at THz frequencies and with ultra-low energies. The lasing medium emission from the cavity is modulated by the presence of a highly absorptive J-aggregate material that is strongly coupled to the cavity [1, 2]. The devices consist of a dielectric mirror, followed by a thermally evaporated layer of the dye DCM (the lasing material) and a 5-nm J-aggregate thin film that is resonantly coupled to the cavity. The cavity is capped with a thermally evaporated silver mirror. The structure is shown in Figure 1.

The cavity is excited non-resonantly with 150-fs pulses (from the pump), which causes lasing emission from the DCM at 600 nm. The emission shows an unusual conical dispersion pattern (Figure 2a) due to the strongly-coupled J-aggregate material in the cavity. A second (gate) pulse, which is resonant with the J-aggregate absorption, is delivered to the sample at a variable time relative to the pump pulse. Upon the excitation of the J-aggregate layer with the gate pulse, the lasing emission is quenched up to 25% (Figure 2b). The modulation of the lasing output occurs only when the pump-gate pulse delay is < 1 ps, permitting operating frequencies of up to 1 THz. The gate pulse energy density required for modulation was ~ 1 fJ/cm². This micro-scale laser modulator is a demonstration of a potentially new class of organic-based, low-power, ultra-fast photonic circuit components. Currently, the role of strong light-matter coupling in the modulation of the lasing is being investigated.

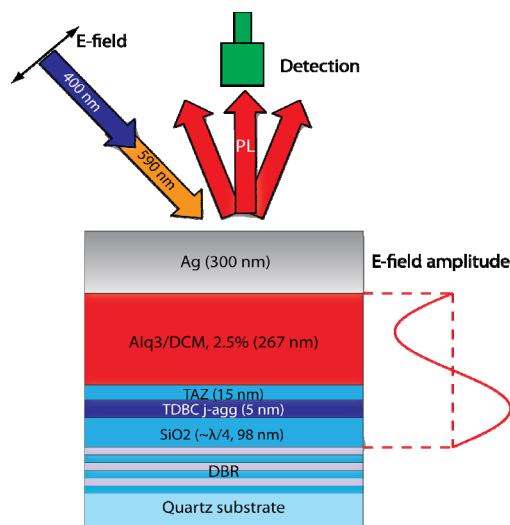


Figure 1: Device structure and diagram of experimental setup.

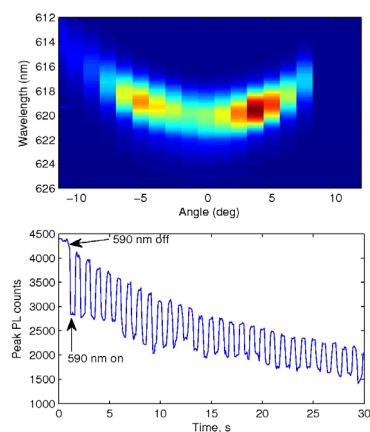


Figure 2: (a) Dispersion of the lasing emission of the cavity. (b) Modulation of the lasing output due to the presence or absence of the low-energy gate pulse.

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4. MEMS Tunable Organic Laser Cavities**Sponsors**

Center for Excitonics, Hertz Foundation, National Science Foundation

Project Staff

G. M. Akselrod, C. Packard, V. Bulović

Standard photolithography-based methods for fabricating micro-electromechanical systems (MEMS) present several drawbacks including incompatibility with flexible substrates and limitations to wafer-sized device arrays. Recently our group has demonstrated a new method for rapid fabrication of metallic MEMS that breaks the paradigm of lithographic processing using an economically and dimensionally scalable, large-area microcontact printing method to define 3D electromechanical structures. Here we utilize this MEMS printing method to create tunable optical cavities, with the ultimate goal of creating an electrically color-tunable organic laser. The device concept is shown in Figure 1. The bottom half of the optical cavity is fabricated by forming ridges of polydimethylsiloxane (PDMS) on a dielectric mirror using a silicon master. The top half of the cavity is independently fabricated by thermally evaporating an organic release layer on a planar PDMS substrate followed by layers of Au and Ag, which act both as the top mirror of the cavity and as the flexible MEMS element. The organic lasing medium (DCM) is evaporated on the metallic layers. This layer structure is stamped onto the PDMS ridges followed by a rapid peel-off, forming the structure shown in Figure 1b.

The photoluminescence from the DCM gain layer under 532-nm excitation shows clear evidence of a vertical optical cavity formed between the dielectric mirror and the Ag flexible membrane, demonstrating an optical microcavity formed by a scalable MEMS printing method. The optical resonances of the device can be varied by applying a bias voltage to the top flexible membrane, thus changing the distance between the mirrors (Figure 1a). This structure paves the way to developing color-tunable organic lasers on flexible substrates over large areas using an economical MEMS fabrication technique.

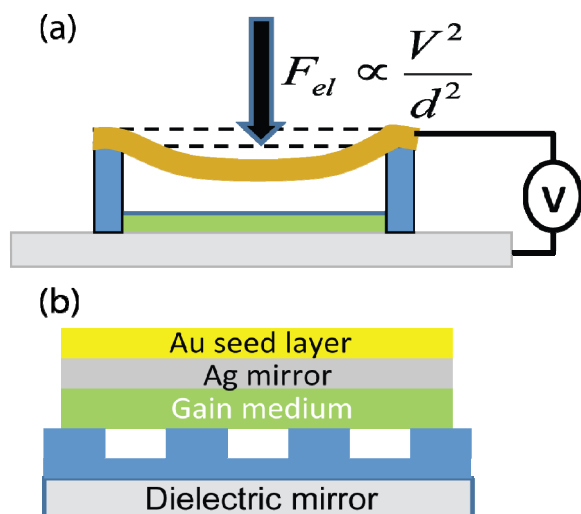


Figure 1: (a) Optical-cavity tuning by biasing a flexible metal membrane. (b) Structure of MEMS tunable laser device.

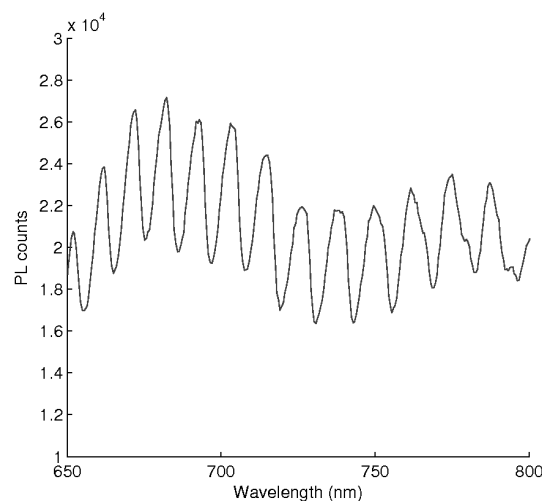


Figure 2: Photoluminescence of the laser dye DCM in a printed optical cavity.

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5. Semi-transparent Solar Cells Based on Colloidal Quantum-dot Films

Sponsors

Department of Energy

Project Staff

P. R. Brown, A. C. Arango, N. Zhao, M. G. Bawendi, V. Bulović

Solar cells based on nanocrystalline quantum dots (QDs) offer a promising solution-processable alternative to conventional photovoltaic technologies. In particular, with a bandgap that may be adjusted simply by varying the size of the nanocrystals, QDs are particularly well-suited for incorporation into multijunction device architectures, with stacked layers of QDs absorbing complementary portions of the solar spectrum. The additional ability to modify the surface chemistry and electronic properties of colloidal QDs via ligand exchange and doping gives them a flexibility unmatched in other materials sets.

As a first step towards the realization of multijunction QD photovoltaics, we have developed a solar cell based on a heterojunction between rf-sputtered zinc oxide (ZnO) and solution-deposited lead sulfide (PbS) QDs employing symmetric, transparent indium tin oxide (ITO) electrodes (Figure 1). Our previous work demonstrated the viability of this symmetric-electrode architecture using cadmium selenide (CdSe) QDs [1]; however, the performance of this device was limited by the low mobility of CdSe QDs. PbS possesses both a higher mobility and a better absorbance match with the solar spectrum than CdSe, and other studies have demonstrated the efficiency of the PbS/ZnO interface in rectifying photocurrent flow [2, 3]. Our results have shown that annealing the device in air decreases the dark current and increases the open circuit voltage and fill factor, but at the expense of a decrease in the short circuit current. Given this device's semi-transparent, symmetric structure, expanding this single-junction device into a stacked multijunction device should be relatively straightforward and will be the focus of our further work.

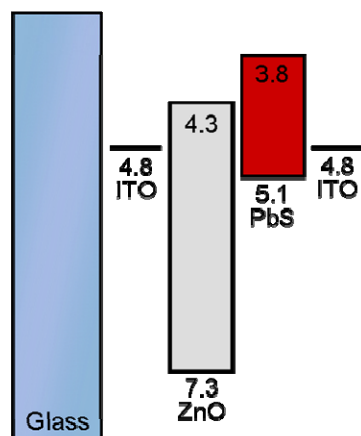


Figure 1: Band diagram of the PbS-ZnO device. The symmetric, transparent ITO electrodes make the device well-suited for stacking in a tandem cell.

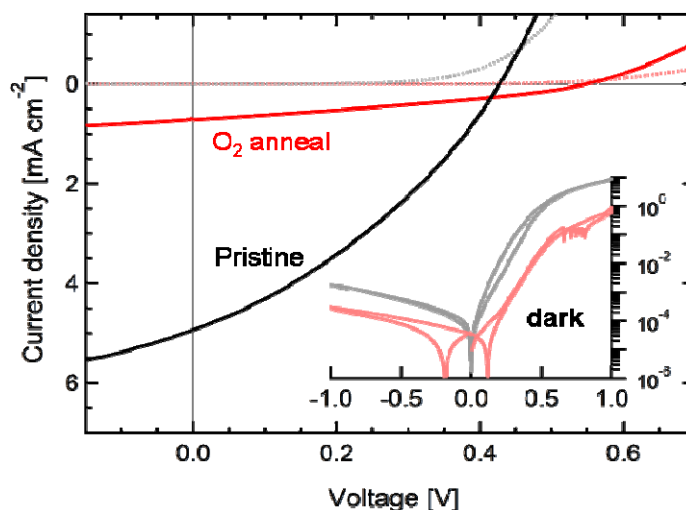


Figure 2: Current-voltage characteristics of the device. The dark current is substantially decreased upon air-annealing, affording an increase in open circuit voltage but a concomitant decrease in photocurrent and efficiency.

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6. Quantum Dot-based Anti-reflective Coatings for Silicon Photodiodes

Sponsors

King Fahd University of Petroleum and Minerals

Project Staff

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Silicon has been the material of choice for large-scale photovoltaics manufacturing due to cost and existing infrastructure and knowledge. Enhancements to the photocell design have been realized through modifications to the active area surface, use of optical-concentration mechanisms, and anti-reflective coatings. Anti-reflective coatings work by reducing the amount of reflected light at the interface through graded index-layering. Silicon has a high reflection coefficient in the UV part of the spectrum and hence low responsivity. We desire to capture this energy and couple the light into the photovoltaic for conversion into electricity. Past research has included investigation of photoluminescent anti-reflective coatings using organics [1]. These luminescent anti-reflection layers absorb in the UV part of the spectrum and demonstrate visible emission, helping to couple light into the active region. Quantum dots offer a similar solution absorbing strongly in the UV and emitting in the visible range, where silicon exhibits a reduced reflectivity

and a concomitant increase in responsivity. In this work, CdSe quantum dots in an epoxy and toluene solution spin-coated and cured on commercially available red-enhanced silicon photodiodes increase photodiode responsivity in the UV compared to that of the original red-enhanced photodiode. Moreover, an increase in the short-circuit photocurrent density by 3% was observed, Figure 1. Application of the coating can be used as a cost-effective solution to enhancing standard silicon photovoltaic performance through the post-processing addition of a luminescent anti-reflective layer.

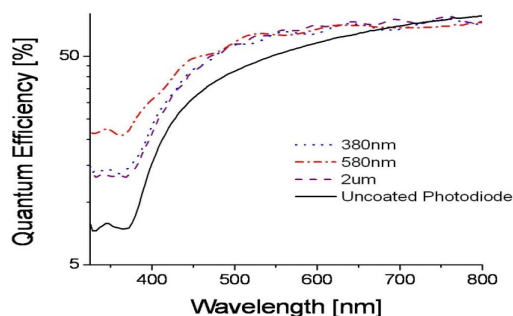


Figure 1: Experimental data for device's external quantum efficiency as a function of wavelength. Responsivity of the photodiode is significantly increased in the UV and across the visible spectrum, allowing for better light-coupling with the device and overall improvement in photocurrent density.

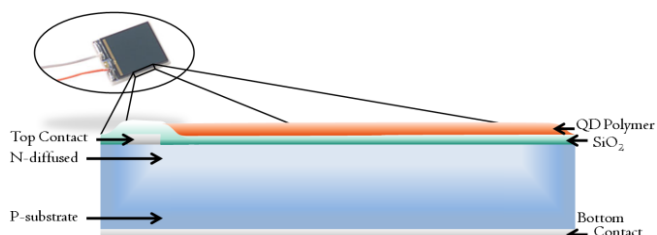


Figure 2: Illustration of QD anti-reflection coated silicon photodiode.

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7. Formation of a Cobalt-based Oxidation Catalyst from Thin-film Cobalt Anodes

Sponsors

National Science Foundation Fellowship

Project Staff

E. R. Young, D. G. Nocera, V. Bulović

Splitting water into molecular oxygen and molecular hydrogen is a compelling strategy for clean energy storage [1]. In order to achieve efficient conversion from water to oxygen or hydrogen fuels, catalytic materials are necessary, and their integration into technological devices is critical. We are currently working with a water-oxidation catalyst that is capable of assisting the transformation from water to molecular oxygen [2]. We report progress towards integration of the catalyst with a thin-film metal electrode surface that may facilitate its utilization in devices.

Eight-hundred-nanometer thin films of cobalt metal are sputter-deposited on a non-conductive glass substrate to serve as electrode scaffolds for formation of the cobalt-based water-oxidation catalyst. The middle one-third of the electrode is masked with an electrochemical masking lacquer positioned at the air-water interface during electrode operation. The catalyst is formed by electrolytic deposition in neutral aqueous solutions of 0.1 M potassium phosphate where the thin films of cobalt serve as the conductive electrodes as well as the source of Co^{2+} cations for formation of the catalyst material. The formation of catalyst films on the thin-film cobalt electrodes is compared to similar films formed from ionic solutions of Co^{2+} on fluorinated tin oxide (FTO) conductive glass electrodes, reported previously [2]. We report that

the chemical composition and the current densities achieved during operation in the catalytic regime are similar for catalytic films on thin-film cobalt and FTO electrodes. The surface morphology of the catalyst film on the thin-film cobalt electrodes is smoother than those found for films formed from Co^{2+} solutions onto FTO electrodes.

This work demonstrates that thin-film cobalt metal electrodes are effective for cobalt-based water-oxidation catalyst formation and successfully eliminate the need for utilizing solutions of Co^{2+} in formation of the catalyst films. Further development of the cobalt electrode is in progress with the goal of increasing the catalytic current output of the catalyst films formed directly on thin-film metal electrodes.



Figure 1: (left) The thin-film cobalt metal electrode is shown with electrochemical masking lacquer (red middle section) and copper tape with conductive epoxy. (right) The thin-film cobalt electrode is shown during operation during catalytic activity. Bubbles forming on the surface of the electrode are molecular oxygen.

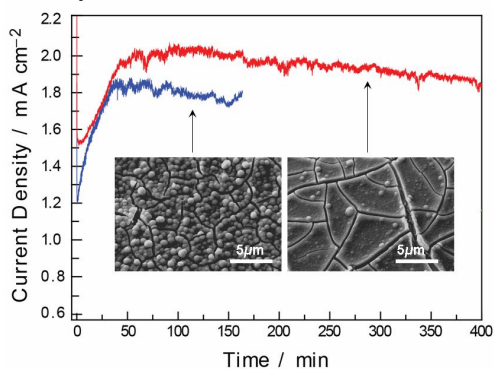


Figure 2: Current density traces for bulk electrolysis at 1.1 V (vs Ag/AgCl) in 0.1M potassium phosphate, pH 7, for (—) catalyst formation on FTO-coated glass anodes with 0.5 mM Co^{2+} and (—) catalyst formation on thin-film cobalt anodes. Both electrodes demonstrate comparable competence in current passage throughout the bulk electrolysis. SEM images at 5000 times magnification of the Co-Pi film formed on each electrode are shown.

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8. Hybrid Organic/Quantum-dot Photodetector with Infrared Sensitivity

Sponsors

Institute for Soldier Nanotechnologies, MIT Center for Materials Science & Engineering

Project Staff

T. P. Osedach, N. Zhao, S. M. Geyer, L.-Y. Chang, D. Wanger, A. C. Arango, M. Bawendi, V. Bulović

Hybrid structures consisting of colloidal quantum dots (QDs) and organic semiconducting materials have attracted a great deal of interest for photodetector device applications. Of particular interest is the prospect of infrared sensitivity with the incorporation of low bandgap QDs such as PbS and PbSe into hybrid organic/inorganic devices. This wavelength range is largely inaccessible to organic materials yet is critical to efficient photovoltaics as well as night vision and biological/chemical imaging applications.

Several hybrid organic/QD photodetector structures have recently been reported to exhibit good performance at infrared wavelengths. One study revealed an efficient charge-transfer mechanism from PbS QDs to the fullerene derivative, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [1]. Another study

described a hybrid device containing PbS QDs that was successfully integrated with amorphous silicon readout electronics to demonstrate the technical feasibility of making QD-based imagers [2].

In this work we investigate charge and exciton dynamics at the PCBM/PbS QD hetero-interfaces through the experimental study of a photoconductor structure comprised of discrete layers of QDs and PCBM. A key feature of this lateral bi-layer device, distinguishing it from other reported hybrid devices, is that it unambiguously isolates the organic/QD hetero-interface as the site for interfacial charge and exciton recombination. Additionally, it affords great flexibility to modify the surface chemistry of the QDs without affecting the charge transport through the organic layer, thus making it a uniquely appropriate platform with which to study properties of the organic/QD hetero-interface.

Our findings elucidate the charge transport and recombination processes present in the PbS/PCBM system and suggest avenues for controlling these processes to optimize photodetector performance. Our optimized devices exhibit external quantum efficiencies above 20% at wavelengths extending to $\lambda=1.4\mu\text{m}$ (see Figure 1) and have frequency bandwidth of $f_{3\text{dB}} > 100\text{kHz}$ (see Figure 1 inset).

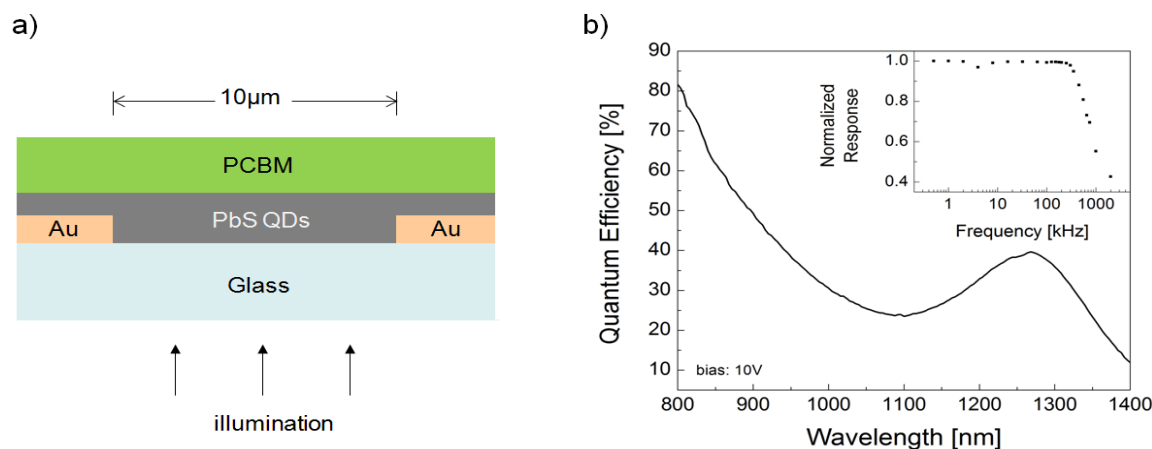


Figure 1: (a) Schematic of PCBM/PbS QD bi-layer photodetector. (b) External quantum efficiency of a device with sensitivity extending to approximately 1400 nm. (inset) Frequency response of a typical device.

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9. CMOS-compatible Molecular Floating-gate Memories

Sponsors

Semiconductor Research Corporation/FCRP - Materials Structures and Devices Center

Project Staff

S. Paydavosi, P. Hashemi, J. L. Hoyt, V. Bulović

Flash memory devices are now entering the sub-50-nm lithography regime. Flash cell scaling is always challenging because of the high electric fields required for the program and erase operations and the stringent leakage requirements for long-term charge storage. The electric-field requirements impose re-

restrictions on the physical scaling of the memory; the diminishing number of stored electrons imposes restrictions on reliability. Overcoming these limitations will require innovations in cell structures and device materials, including proposals for replacing the polysilicon floating gate by segmented charge storage elements. With discrete charge storage, the impact of a defect is limited only to charge stored in its proximity and not to leaking of the conducting floating gate.

This study investigates charge-storage behavior in a series of molecular thin films embedded in metal-oxide-semiconductor (MOS) structures with SiO_2 and Al_2O_3 as the tunneling and control oxides, respectively. By comparing performance of different devices, we identify the molecular thin-film characteristics best suited for design of floating-gate memories. We fabricate capacitive memory structures using archetypical molecular thin films with different charge-storage energy levels and charge mobility including 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI), tris-(8-hydroxyquinoline) aluminum (Alq_3), and fullerene (C_{60}).

The stored charge densities are determined by measuring the shift in the flat band voltage of molecular-film-containing capacitors. Data shows that charge retention times are improved for molecular films with lower carrier mobility, which for the first time confirms the stated operational benefit of the nano-segmented floating-gate structures, i.e., that lower charge mobility in the nano-segmented floating gate inhibits stored charge loss.

The initial results show device durability over 10^5 program/erase cycles, with a hysteresis window of up to 12.8V, corresponding to charge storage density as high as $1.3 \times 10^{13} \text{ cm}^{-2}$.

As the next step we are working on fabrication of CMOS-compatible organic memory transistors using gate-last fabrication process, in which source and drain regions are defined using a dummy poly gate that is removed during the process.

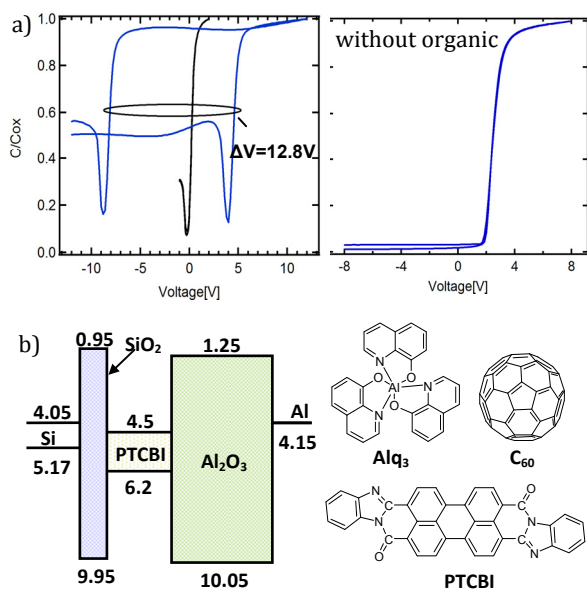


Figure 1: a) The C-V characteristic of devices with PTCBI/ C_{60} and without organic layer, and b) energy-band diagram and chemical structure of organic materials.

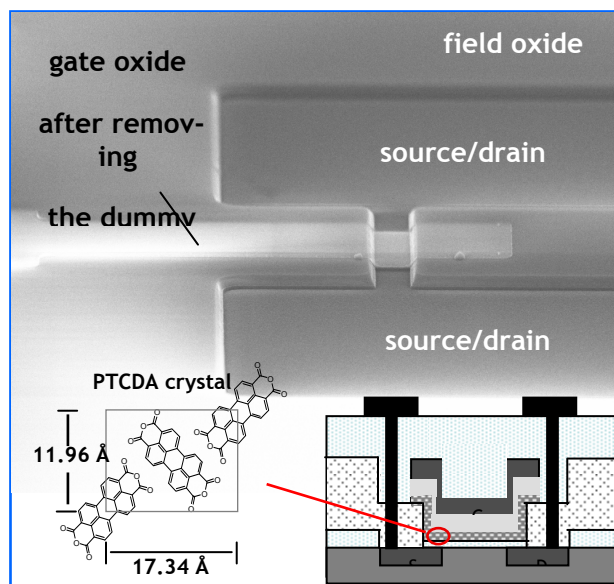


Figure 2: SEM image of memory transistor after removing the dummy poly gate and schematic cross section of the transistor.

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10. Experimental and Theoretical Investigation of Resonant-Cavity Enhanced Colloidal Quantum-dot Light-emitting Diodes

Sponsors

MIT Institute for Soldier Nanotechnologies, DOE Center for Excitonics at MIT

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Quantum-dot light-emitting diodes (QD-LEDs), which capitalize on the excellent color saturation and high photoluminescence efficiencies offered by quantum dots (QDs), promise to be part of future generations of display technologies [1]. The goal of our project is to integrate the QD-LED into a resonant cavity (RC) and enhance the intensity and the directionality of the QD electroluminescence (EL) akin to Schubert's study of RC GaAs LEDs [2]. This enhanced QD emission may 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 alternating layers of material with high and low indices of refraction. The Ag electrode on the top of QD-LED constitutes the other cavity mirror of the resonant cavity. 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).

To better understand and optimize the device, we are currently modeling the device architecture to simulate the effect of the resonant cavity on the emission of the QD-LED. Our approach builds from first principles, calculating the optical modes of the system to deduce the coupling strength between the vacuum electric field and the QD transition dipole and then applying Fermi's golden rule to determine the spontaneous emission rate of the QDs.

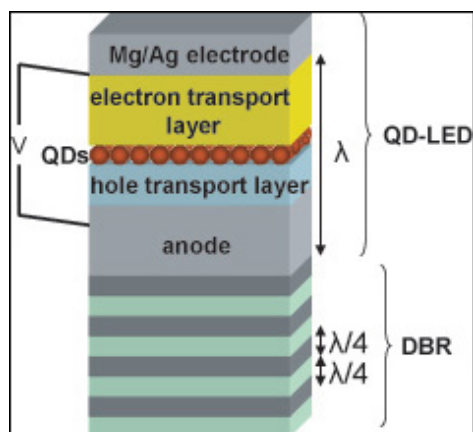


Figure 1: Schematic of RC QD-LED.

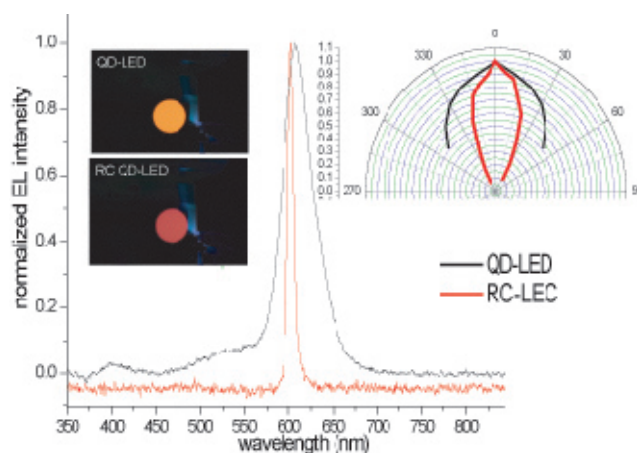


Figure 2: Comparison of EL spectra, images, and angular emission profiles of RC QD-LED and QD-LED. The RC QD-LED exhibits marked narrowing.

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11. Two-dimensional Fourier Transform Electronic Spectroscopy of J-aggregates

Sponsors

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J-aggregates are aggregates of organic molecules whose optical properties are characterized by a red-shifted, narrowed absorption band and a larger oscillator strength compared to its smaller molecular components [1]. The fundamental optical excitation in J-aggregates, the Frenkel exciton, can couple strongly to an optical cavity photon, as in room-temperature, polariton-based organic light-emitting diodes [2]. Exploiting the strong coupling limit in J-aggregate/microcavity-based devices requires a narrow exciton line-width that is sensitive to homogeneous and inhomogeneous broadening processes. We investigated exciton dephasing and relaxation of J-aggregates suitable for microcavity-based devices using two-dimensional Fourier transform (2D FT) electronic spectroscopy.

The 2D FT electronic spectroscopy measurement involves focusing four femtosecond laser pulses into the J-aggregate sample with varying pulse delays and wave vectors and interferometrically detecting the stimulated emission of the exciton with respect to different pulse delays [3]. The signal is Fourier-transformed with respect to the time delay between the first two pulses (the absorption period) and the last two pulses (the emission period) to yield the 2D spectral surfaces shown in Figure 1 for different exciton relaxation times, T , which is defined by the time delay between the second and third pulses. At $T = 0$ (Figure 1, left) the main spectral features are aligned along the $y=x$ diagonal line, which reveals the ratio of inhomogeneous to homogeneous broadening of the exciton resonance, since the exciton absorption and emission are strongly correlated. As the exciton relaxation time is increased to $T = 860$ fs (Figure 1, right), the spectral features tilt toward the absorption axis, which reveals a loss of correlation since the

exciton can sample different environments as it relaxes.

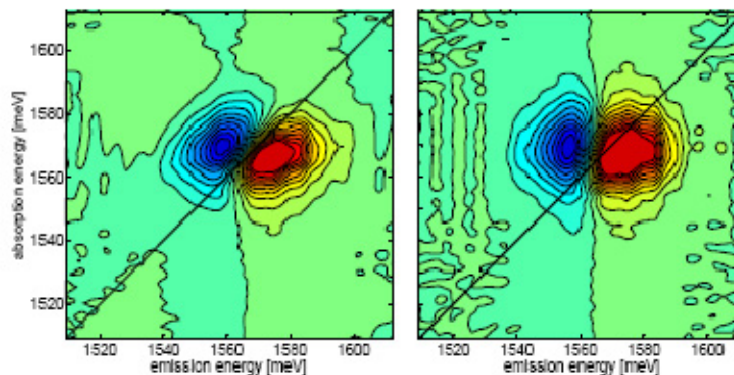


Figure 1: Correlation spectra of a J-aggregate in solution at room temperature for exciton relaxation times $T = 0$ (left) and $T = 860$ fs (right). Positive-going features (red) indicate induced absorption into the two-exciton manifold, and negative-going features (blue) indicate exciton bleaching. The change in the nodal angle during the exciton lifetime is related to the rate of spectral diffusion of the exciton.

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12. High-efficiency Infrared Colloidal Quantum-dot Light-emitting Diodes

Sponsors

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While boasting high performances and long lifetimes, the associated fabrication and materials costs of established infrared (IR) technologies (such as inorganic light-emitting diodes (LEDs) and lasers) preclude their use in cost-constrained, large-area applications [1]. Solution-processable LEDs promise lower manufacturing costs and compatibility with a variety of (flexible) substrates. In the IR region, the incorporation of solution-processable IR light-emitters into on-chip optoelectronic integrated circuits is an alluring possibility [1]. Optical diagnosis in biologically transparent windows at 800, 1100, and 1300 nm could also be performed using large-area IR emitters [2]. However, solution-processable molecular and polymeric organic LEDs have limited extendibility into the IR region owing to negligible optical activity beyond 1 μm [1]. In contrast, colloidal quantum-dot LEDs (QD-LEDs) combine the thin film processability of organic materials with the tunable optical properties conferred by QD size control. Additionally, the colloidal PbS QDs employed here can be reproducibly synthesized with a narrow size distribution, demonstrate greater stability [3] than PbSe (on which several previously reported devices have been based [1]), and exhibit a remarkably high thin-film absolute photoluminescence (PL) efficiency of 18 to 20 %.

We report efficient IR electroluminescence (EL) from large-area (mm^2 in size) LEDs comprising solution-deposited colloidal PbS QDs sandwiched between organic hole- and electron-transporting layers (HTL/ETL) deposited at room temperature, as shown in the inset of Figure 1. Spin-casting of a blend solu-

tion of QDs and a hole transporting material yields a QD monolayer at the surface via a spontaneous phase-segregation process previously reported by our group [4] (see Figure 2). IR EL is observed at turn-on voltages as low as 4 V and closely resembles the corresponding QD PL spectrum (Figure 1).

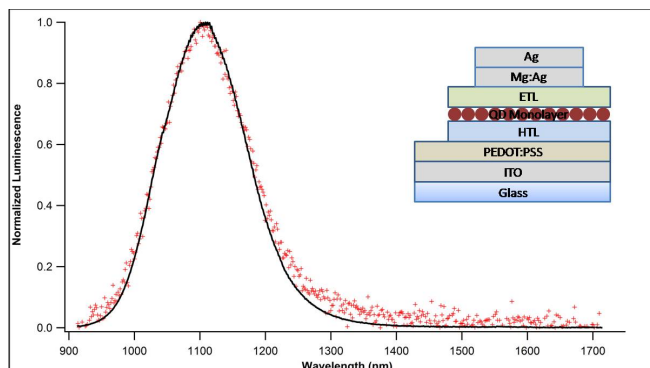


Figure 1: Normalized infrared electroluminescence (black, solid) and photoluminescence (red, crosses) spectra of a PbS QD-LED centered at 1.11 μm . The inset shows the general device structure.

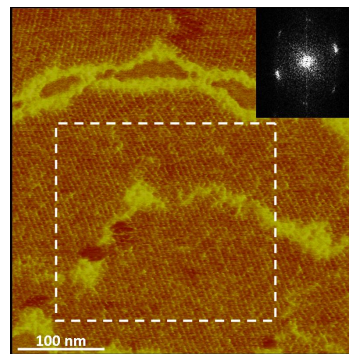


Figure 2: Tapping-mode Atomic Force Microscope (AFM) phase image of nearly complete monolayer coverage of an organic HTL by ~ 4 nm PbS QDs. QDs have the tendency to pack into regular hexagonal arrays. The inset illustrates a two-dimensional spatial Fourier Transform of the area delineated by the dashed box, revealing the expected six-point pattern.

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13. Colloidal PbS Quantum Dots Solar Cells with High Fill Factor

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We fabricate PbS colloidal quantum-dot (QD)-based solar cells using a fullerene derivative as the electron transporting layer (ETL). A thiol treatment and oxidation process are used to modify the morphology and electronic structure of the QD films, resulting in devices that exhibit an open-circuit voltage (V_{oc}) of

0.47 V and a fill factor (FF) of 62%. These values are the highest among published VOC and FF for PbS and PbSe-QD-based solar cells to date. The power-conversion efficiency reaches 1.3% under 1-sun AM1.5 test conditions and 2.4% under monochromatic infrared ($\lambda = 1310$ nm) illumination. A consistent mechanism for device operation is developed through a circuit model and experimental measurements, shedding light on new approaches to the optimization of solar-cell performance by engineering the interface between the QDs and the neighboring charge-transport layers.

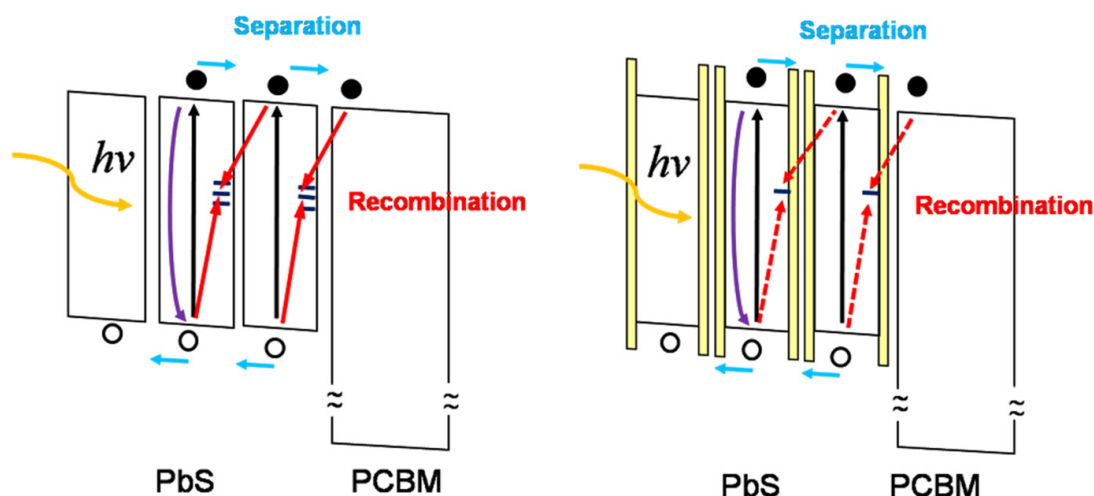


Figure 1 Illustration of the charge-flow mechanism in the pristine (left) and air-annealed (right) PbS QD/PCBM devices. The black arrows denote the exciton generation process, the purple arrows denote the geminate electron-hole pair recombination process, the blue arrows denote the charge separation process, and the red arrows denote the bimolecular recombination process (assisted by midgap states). The thin wider band gap layers (yellow) that surround each QD in the right figure represent the oxide compounds, and the dashed red arrows indicate a suppressed charge recombination via the bimolecular process.

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Ph.D. Thesis:

A. Arango, "High Open-Circuit Voltage in Heterojunction Photovoltaics Containing a Printed Colloidal Quantum-Dot Photosensitive Layer" (November 2009, Electrical Engineering and Computer Science, supervised by V. Bulović)

V. Wood, "Electrical Excitation of Colloidally Synthesized Quantum Dots in Metal Oxide Structures" (October 2009, Electrical Engineering and Computer Science, supervised by V. Bulović)

J. Ho, "Organic Lateral Heterojunction Devices for Vapor-phase Chemical Detection" (June 2009, Electrical Engineering and Computer Science, supervised by V. Bulović)

M. S. Bradley, "Engineering J-Aggregate Cavity Exciton-Polariton Devices" (June 2009, Electrical Engineering and Computer Science, supervised by V. Bulović)

P. Anikeeva, "Physical Properties and Design of Light-Emitting Devices Based on Organic Materials and Nanoparticles" (February 2009, Materials Science and Engineering, supervised by V. Bulović)