Final Report

2-08-12

Quantum Dot Light Emitting Diode

Work Performed Under Agreement:
DE-FC26-06NT42864

Submitted By:
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Submitted To:
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PROJECT DESCRIPTION

1. Project Title:
   Quantum Dot Light Emitting Diode

2. Performer:
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   Matthew Holland, Eastman Kodak
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   Prof. Paul McEuen, Cornell University
   Dr. Yaqiong Xu, Cornell University
   Prof. Todd Krauss, University of Rochester
   Dr. Xiaoyong Wang, University of Rochester
   Prof. John Silcox, Cornell University
   Sara Maccagnano, Cornell University

5. Technology Focus:
   Core

6. Relevant Subtask Priority Area:
   1.1.2: High Efficiency semiconductor materials
7. **Schedule/Budget Overview:**

Through the first two quarters of budget period #1, we are underspending our budget by 8%.

<table>
<thead>
<tr>
<th></th>
<th>Start Date</th>
<th>End Date</th>
<th>Government Share</th>
<th>Performer Share</th>
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<tbody>
<tr>
<td><strong>Budget Period 1</strong></td>
<td>(08/01/06)</td>
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<td>(07/31/08)</td>
<td>$1,161,000</td>
<td>$775,00</td>
<td>$1,936,00</td>
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8. **Project Objective:**

Create low cost coatable inorganic light emitting diodes, composed of quantum dot emitters and inorganic nanoparticles, which have the potential for efficiencies equivalent to that of LEDs and OLEDs and lifetime, brightness, and environmental stability between that of LEDs and OLEDs. At the end of the project the Recipient shall gain an understanding of the device physics and properties of Quantum-Dot LEDs (QD-LEDs), have reliable and accurate nanocrystal synthesis routines, and have formed green-yellow emitting QD-LEDs with a device efficiency greater than 3 lumens/W, a brightness greater than 400 cd/m², and a device operational lifetime of more than 1000 hours. Thus the aim of the project is to break the current cost-efficiency paradigm by creating novel low cost inorganic LEDs composed of inorganic nanoparticles.

9. **Technical Approach and Work Plan:**

Our project is driven by the desire to combine the best attributes of LED and OLED devices into a single technology. LEDs currently enjoy long lifetimes, high brightness, and very good efficiencies. Typically, an individual device emits light of a particular color. Because the semiconductor layers in LEDs need to be crystalline, they are typically grown by expensive ultra-high vacuum techniques. Thus, despite the impressive performance characteristics of the LEDs, low cost remains an elusive feature. Because OLED device layers are amorphous, OLEDs enjoy the benefits of lower manufacturing cost, the ability to emit multiple colors from the same device, and the promise of flexible lighting. In comparison to LEDs, OLEDs have reduced brightness (mainly due to smaller carrier mobilities), shorter lifetimes, and require expensive encapsulation for device operation.

Looking at the two light emitting diode technologies, a means to overcome the shortcomings associated with each technology is to introduce a new technology that is LED-like in some aspects and OLED-like in other properties. The technology should be based on inorganic components to enable higher brightness (larger mobilities), longer lifetimes, and reduced encapsulation requirements. In addition, the layers should be polycrystalline, which would enable low manufacturing costs (in addition to multicolor
emission from a single device), and brightnesses between those of LEDs and OLEDs. QD-LEDs, formed entirely from colloidal inorganic nanoparticles, have the potential to meet these criteria.

Emissive inorganic quantum dots are nanometer-scale inorganic semiconductor particles that are quantum confined in three dimensions [1]. The prototypical example is the CdSe quantum dot that can be made to emit from 465 to 640 nm [2] by varying the diameter (1.9 to 6.7 nm) of the nanocrystal. Low cost nanoparticles can be formed by chemical synthetic methods [3]. The most common method is decomposition of molecular precursors at high temperatures in coordinating solvents [4]. The nanoparticles resulting from these methods can be passivated by an outer shell of organic ligands that enable the formation of non-scattering colloidal dispersions in a variety of organic solvents [5]. Nanoparticle films can then be formed by using low cost deposition processes, such as spin casting [5], drop casting [6], or inkjetting to deposit the nanoparticle colloidal dispersions.

Recently, a mainly inorganic LED was constructed [7] by sandwiching a monolayer thick core/shell CdSe/ZnS quantum dot layer between vacuum deposited n- and p-GaN layers. The resulting device had a poor external quantum efficiency of 0.001 to 0.01%, that could be associated with the organic ligands of trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) which were reported to be present post growth. Organic ligands are insulators and would result in poor electron and hole injection into the quantum dots. A means for avoiding direct injection into the quantum dots and to obtain reasonable efficiencies (1.5 cd/A) is to form a hybrid emitter, containing quantum dots and organic emitter species [8]. Emission occurs as a result of e-h recombination on the organic emitters followed by Forster energy transfer to the quantum dots. Regardless of future improvements in efficiency, these hybrid OLED devices suffer from the drawbacks associated with pure OLED devices: low carrier mobilities in the organic and quantum dot layers and poor environmental stability of the organic components [9].

![Schematic of quantum dots and conductive nanoparticles composing the emitter layer](image)

**Fig. 1:** Schematic of quantum dots and conductive nanoparticles composing the emitter layer
As discussed above, typical quantum dot-based emitter layers are luminescent, but insulating. Figure 1 schematically illustrates an emitter layer that is simultaneously luminescent and conductive. The concept is based on co-depositing small (< 2 nm), conductive nanoparticles (such as ZnS) along with core/shell quantum dots to form the emitter layer. The conductive nanoparticles need to be wide band gap semiconductors, such as ZnS, to enable efficient injection of the electrons and holes into the quantum dot shells.

The deposition is performed by either spin or drop casting a colloidal dispersion containing appropriate fractions of the conductive nanoparticles and the quantum dots. A subsequent inert gas (Ar or N$_2$) anneal step (250 – 300°C for 30-60 minutes) is used to sinter the smaller nanoparticles amongst themselves and onto the surface of the larger quantum dots (at least 8-9 nm). The low melting temperature of nanocrystals (relative to their bulk counterparts) was reported previously [10]. Sintering of the nanoparticles results in the creation of a continuous, conductive semiconductor matrix. Through the sintering process this matrix is also connected to the quantum dots, providing a conductive path from the edges of the emitter layer, through the semiconductor matrix to each quantum dot, where the electrons and holes recombine in the quantum dot cores. Encasing the quantum dots in the conductive semiconductor matrix has the added benefit of protecting the quantum dots environmentally from the effects of both oxygen and moisture.

Following the anneal step, the quantum dots would be devoid of an outer shell of organic ligands (for colloidal based quantum dots, the main function of the organic ligands are to passivate the surface states and to stabilize the colloid). For the case of CdSe/ZnS core/shell quantum dots, having no outer ligand shell would result in a loss of free electrons due to trapping by the shell’s unpassivated surface states [2]. Consequently, the annealed core/shell quantum dots would show a greatly reduced quantum yield compared to the unannealed dots. To avoid this situation, the ZnS shell thickness needs to be increased until the core/shell quantum dot electron and hole wavefunctions no longer sample the shell’s surface states. It can be calculated [11] that the thickness of the ZnS shell needs to be at least 5 monolayers thick in order to negate the influence of the electron and hole surface states.

Both the contact and transport layers are composed of inorganic nanoparticles. As discussed by Gur et al. [12], even when the organic ligands are removed from the surfaces of the nanoparticles and the particles are sintered together to increase the crystalline domain size of the layer, nanoparticle films can remain highly insulating. To avoid this problem the layers need to be doped. Our approach is to use a combination of novel in-situ and ex-situ doping schemes to incorporate either donor or acceptors atoms into our contact and transport layers. In general, in-situ doping involves incorporating dopant atom monomer species during the synthesis of the nanoparticles. Even though many groups worldwide [13] have added dopants atoms to nanoparticles (during synthesis) to modify their emission or magnetic properties, none has successfully added dopant atoms to modify the conductivity properties of the resulting nanoparticle-based film layers. The classic ex-situ doping schemes are ion implantation and metal atom diffusion (from a surface or vapor source). Neither one is low cost. Our approach has been to devise a novel nanoparticle-based scheme to ex-situ dope the contact and transport layers.
The three key thrusts for the project are creating an efficient emitter layer (which is simultaneously luminescent and conductive), doping the transport and contacts layers, and combining the various layers to form LED pin diodes. To accomplish this, the project (2 years in duration) is broken up into 5 main tasks. In the first year the tasks are emitter layer optimization, transport (contact) layer optimization, and bringing up the microscopic device characterization techniques. For year 2, the tasks are formation of ohmic contacts (one of them being transparent) and construction (and optimization) of the QD-LED devices. The Kodak team is responsible for all of the nanoparticle synthesis and device formation. The majority of macroscopic device characterization also occurs at Kodak, such as, X-ray diffraction (XRD) analysis of device layers; quantum efficiency measurements; resistivity measurements; CV measurements; and IV, LI, and lifetime testing of devices (making use of the infrastructure built up at Kodak for OLED device characterization). UR is responsible for single molecule optical characterization (time resolved) of the quantum dots (either isolated or in the emitter layer). Cornell (McEuen) is responsible for scanned probe microscopy (using AFM tips) of the device layers, the device interfaces, and of recombination events occurring in the emitter layer. In addition, they will perform high frequency measurements of the devices both at room and cryogenic temperatures. Extensive use will be made of the Cornell NNF facility for performing device processing as needed. Cornell (Silcox) is responsible for STEM and EELS (electron energy loss spectroscopy) measurements of the nanoparticles (both emissive and non-emissive) and emitter layer. Routine TEM screening will also be performed at Kodak.

Emitter layer optimization involves synthesizing appropriate core/shell quantum dots, forming conductive nanoparticles, and combining them together to create an efficient emitter layer (tested by optical means). TEM, STEM, EELS, and single molecule optical spectroscopy will be extensively used to characterize the quantum dots, the conductive nanoparticles, and the combination of the two in the emitter layer.

The task of transport layer optimization involves formulating novel schemes for in-situ and ex-situ doping of the nanoparticles in the transport and contact layers. Resistivity and CV measurements will be the main characterization tools. Work will also be directed to boosting the mobility of the layers by appropriate variations in the type and sizes of the nanoparticles. Hall effect and XRD measurements will be the main macroscopic characterization tools. Scanned probed microscopy will be used to characterize the layers on a microscopic scale.

Task 3 involves bringing up the single molecule time resolved optical spectroscopy equipment and adding optical characterization to the scanned probed microscopy unit. In addition, the initial horizontally-oriented device structures will be fabricated to enable scanned probed microscopy of devices. The fabrication will occur at the Cornell NNF facility.

Ohmic contact formation involves using the doped contact layers from task 2 to form ohmic contacts with appropriate opaque and transparent conductors. Only one of the contacts needs to be transparent. 2-point probe, transmission line, and scanned probed microscopy measurements will be used to characterize the contacts.

The final major task of QD-LED device formation and characterization involves combining (and optimizing) all of the component layers to form an LED pin diode. The high frequency test stations at Cornell will be used to characterize the devices from DC to
THz frequencies and from room temperature to cryogenic temperatures. Special devices will also be formed to determine if problems exist at the interfaces between the device layers.

**Project Timeline**

<table>
<thead>
<tr>
<th>Task #</th>
<th>Description</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Set up single molecule luminescent equipment</td>
<td>Jan. 2007</td>
</tr>
<tr>
<td>2</td>
<td>Perform microscopic electro-optical measurements on initial device layers</td>
<td>Jan. 2007</td>
</tr>
<tr>
<td>3</td>
<td>Establish a SILAR-based growth technique to form green-yellow emitting quantum dots with quantum yields greater than 75%</td>
<td>Apr. 2007</td>
</tr>
<tr>
<td>4</td>
<td>Create optimized emitter layers with IQE (optically pumped) in air greater than 30% and resistivity lower than $10^8$ ohm-cm</td>
<td>Aug. 2007</td>
</tr>
<tr>
<td>5</td>
<td>Use dopant incorporation and particle size modifications to create n-type and p-type transport layers with resistivity lower than 100 ohm-cm</td>
<td>Aug. 2007</td>
</tr>
<tr>
<td>6</td>
<td>Use a combination of experimental and theoretical work to predict the ultimate radiative recombination efficiency of the quantum dot emitter layer</td>
<td>Aug. 2007</td>
</tr>
<tr>
<td>7</td>
<td>Form n- and p-type ohmic contacts ($&lt; 1$ ohm-cm$^2$)</td>
<td>Nov. 2007</td>
</tr>
<tr>
<td>8</td>
<td>Form transparent n- or p-type ohmic contact</td>
<td>Jan. 2008</td>
</tr>
<tr>
<td>9</td>
<td>Create green-yellow QD-LED device with brightness greater than 400 cd/m$^2$ and device efficiency greater than 3 lm/W</td>
<td>Aug. 2008</td>
</tr>
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</table>

10. **Progress-to-Date:**

To date progress has been made in all five task areas, even though tasks 4 and 5 were not scheduled to be worked on until the second budget period.

With regard to emitter layer optimization, work was performed on synthesizing high efficiency and robust core/shell quantum dots, synthesizing appropriate conductive nanoparticles, and combining them together to form emitter layers with high, optically-pumped IQEs. We can routinely form core/shell quantum dots with quantum yields in the 75-85% range. We determined that the SILAR-based growth method for forming quantum dots is not robust and, hence, the methodology was abandoned. Appropriate conductive nanoparticles were also formed. Combining the dots and nanoparticles to form the emitter layer, optically pumped EQEs in the 70-75% range were measured following no anneal and after an anneal to boil off the insulating organic ligands. Hence the dots are robust even with no passivating organic ligands on their surfaces. These results also show that we can form solid films containing quantum dots and lose very little in quantum yield compared to the values in solution (thus the dots don’t suffer from proximity quenching). To form a conductive emitter layer, the layer is annealed at temperatures between 250 and 300º C. Optically pumping the resulting layer yields highly visible emission viewable in bright room lights (EQE values will be available at the review in June). Unlike typical quantum dots, our engineered dots still maintain high quantum yields (50% range) and minimal shifts in emission peaks following 300º C anneals of the quantum dots in solution. Single molecule blinking and anti-bunching
measurements were also performed on our core/shell quantum dots. For the some of the dots, the blinking on times are greater than 1 hour and their PL decay lifetimes are 4 ns (see Fig. 2). In comparison, the longest reported on times for colloidal quantum dots are ~1 minute and the lifetimes are ~20 ns. The values we obtained are more reminiscent of MBE (MOCVD) grown quantum dots that remain on for hours and whose lifetimes are 1-2 ns. Producing colloidal quantum dots with our blinking and lifetime characteristics is highly desirable since it implies that our dots have very good surfaces (surface state trapping is minimized) and lack internal defect traps.

![Coincidence Counts](image)

**Fig. 2:** Anti-bunching results for our (a) core/shell dots and for typical (b) high quantum yield (85%) dots.

For the transport layer task we invented a novel in-situ doping process and demonstrated a two order of magnitude decrease in the resistivity of the n-type contact layer that is composed solely of doped nanoparticles. As a result we are the first group worldwide to demonstrate in-situ doping (donors or acceptors) of nanoparticles. Using the in-situ doping process the resistivity of the n-contact layer fell to $10^5$ ohm-cm. With regard to ex-situ doping, we developed a novel, low cost, nanoparticle-based ex-situ doping process that yielded a factor of 10 lowering in the resistivity of the p-type contact layer. As a result of these two doping processes, ohmic contacts were formed (as discussed below) to both contact layers. Lastly, by properly annealing the p-contact layer, its resistivity was lowered to 70 ohm-cm.

![Voltage Distribution](image)

**Fig. 3:** ac-EFM scan of the voltage distribution across the p-type contact layer contacted by two anodes.
Task 3 was completed. Both the single molecule time resolved optical spectroscopy system is in place, as is the optical addition to the scanned probed microscopy unit. As an example of the application of ac-EFM (electric field microscopy), Fig. 3 shows the voltage profile resulting from a scan across a sample containing the p-type contact layer sandwiched by two anodes. The voltage profile shows that the contacts are ohmic and the contact resistance is small. Also, the resulting microscopic resistance of the layer agrees well with the value derived from macroscopic 4-point probe measurements.

As a result of the doping work, ohmic contacts were formed to both the n- and p-type contact layers. In addition, a transparent cathode was constructed (70% transmission at 560 nm) that formed an ohmic contact to the n-contact layer. For all three contacts, contact resistance measurements will be made at a later date.

In preparation for the QD-LED device construction, diodes were formed composed of the n- and p-contact layers. The results for one of the diodes are given in Fig. 4. The IV curve in Fig. 4 demonstrates that reasonable IV curves can be formed from our doped nanoparticle layers and that there are no serious problems at the interfaces between the various layers.

![IV curve for nanoparticle-based pn diode](image)

**Fig. 4:** Diode composed of doped n-contact layer on doped p-contact layer, with the two formed on a p-Si substrate.

11. **Technical Barriers/Problems:**

There might be some issue with regard to hitting the target of both transport layers having resistivities less than 100 ohm-cm. Since the goal was moved to the end of the year (see next section), there remains sufficient time to optimize the in-situ and ex-situ doping processes so as to meet the resistivity targets. As such, this alert is more of a cautionary statement.

For the emitter layer, we anticipate possible issues with regard to injection of electrons and holes into the core/shell quantum dots (perhaps the free carriers being trapped at the interfaces between the dot surfaces and the conductive nanoparticles). To minimize this potential problem we are reformulating our conductive nanoparticles and
annealing processes so as to minimize the number of trap states formed at the interfaces between the dots and the nanoparticles. In addition, we are moving quickly to begin forming electroluminescent devices containing our emitter layers in order to test more rigorously the e,h injection issue. Electrical injection studies will begin in June.

12. **Milestones/Deliverables:**

The technical milestones are listed in the project timeline included in section 9. At this time we are on target for the majority of our goals. As discussed in the previous sections, the quantum dot quantum yield goal was exceeded, we are progressing well towards our goal of producing a 30% IQE (optically pumped) emitter layer, we formulated and demonstrated novel processes for in-situ and ex-situ doping of the transport layers, and we brought up the time resolved optical spectroscopy and scanned probed microscopy capabilities. In addition, we made significant progress in meeting our ohmic contact goals for the second year of the project.

We made the decision recently to focus more attention on improving the IQE of the emitter layer rather than meeting the near-term goal for the transport layers (resistivity less than 100 ohm-cm). As a result our initial QD-LED devices will likely be formed on p-type GaN epi so that holes will be injected into the emitter layers from good quality p-transport layers. Corresponding to this priority rearrangement, the transport layer resistivity goal will be delayed to the end of the year. Since forming quality emitter layers is the key to the device, we believe we made the proper decision in rebalancing our current focus.

Our first year deliverables are an air stable emitter layer having an optically pumped (400 nm excitation) IQE greater than 30%; and, p-type and n-type transport layers having resistivities less than 100 ohm-cm. Currently, we expect to provide the first deliverable on time, while, as discussed above, the second deliverable will be postponed to the end of the year.

13. **Project Team/Capabilities:**

As discussed above the project has been split up so that Kodak personnel work mainly on nanoparticle synthesis, device formulation, and macroscopic characterization; while, the university teams work on microscopic characterization of the nanoparticles and device layers. This split was a natural one given the expertise of the university team members in their particular characterization areas. More specifically, Dr. Kahen is the PI for the project. Kahen has over 14 years of experience in various aspects of design, fabrication, and testing of optoelectronic devices, such as LEDs and lasers (both organic and inorganic). For ten of those years, he was the lead scientist and project manager for the research efforts. In addition to numerous journal articles and conference talks, he has over 25 US patents associated with optoelectronic research projects. Besides managing the project, Kahen will be involved in all aspects of design, growth, and characterization of the nanoparticles and QD-LED devices. The other Kodak team members are M. Holland, full time in device construction, X. Ren, half time in nanoparticle synthesis, and R. Young, half time in device characterization.
Prof. McEuen is one of the world’s leading experts on the transport properties of nanoscale conductors, including nanocrystals, nanotubes, and single molecules. In the past decade, he has published 11 papers in Science and Nature alone on these topics. His full time postdoc (Y. Xu) will use the suite of transport and scanned probe techniques he has developed to understand transport, trapping, and recombination on the nanometer scale. Prof. Krauss is a world leader in the area of semiconductor nanocrystals, semiconductor nanocrystal photonic devices, and their characterization, having published over 30 papers in this area in the last several years. Krauss also is an expert in optical spectroscopy and microscopy down to the single nanoparticle level. His full time postdoc (X. Wang) will use single molecule time resolved optical spectroscopy to measure the surface characteristics and recombination kinetics of the quantum dots. Prof. John Silcox is a pioneer in the use of STEM and EELS in characterizing solid-state materials. His 1/3 time graduate student (S. Maccagnano) will use STEM and EELS to characterize the size, shape, composition, and crystalline characteristics of the nanoparticles (both isolated and in the device layers).

References: