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Multi-color colloidal quantum dot based light emitting diodes micropatterned on silicon hole transporting layers

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Received 23 January 2009, in final form 30 March 2009
Published 18 May 2009
Online at stacks.iop.org/Nano/20/235201

Abstract

We present a colloidal quantum dot based light emitting diode (QD-LED) which utilizes the p-type silicon substrate as the hole transporting layer. A microcontact printing technique was introduced to pattern self-assembled CdSe/ZnS QD films, which allowed creation of an LED with well-defined geometry suitable for monolithic integration on silicon substrates. Our QD-LED consists of multi-layers of inorganic materials: a combination of Au (thickness: 5 nm) and Ag (12 nm) as the cathode, a ZnO:SnO2 mixture (ratio 3:1, 40 nm) as the electron transporting layer, CdSe/ZnS QDs as the light emission layer, 1 nm SiO2 as an energy barrier layer, and p-type silicon as the hole transporting layer. These printed QD-LEDs are capable of multi-color emission peaked at wavelengths of 576 nm, 598 nm, and 622 nm, corresponding to sizes of the embedded QDs with the diameters of 8.4 nm, 9.0 nm, and 9.8 nm respectively. The optimal thickness of the quantum dot layers needed for light emission is characterized using atomic force microscopy: for 8.4 nm QDs, the value is 33 nm (+5 nm) or ∼4 ML (monolayers). Larger turn on voltages were measured (2, 4 and 5 V) for the smaller average particle diameters (9.8 nm, 9.0 nm and 8.4 nm, respectively). The mixture ratio of Zn and Sn was optimized (40% Zn and 25% Sn) to maintain proper hole–electron recombination at the QD layer and avoid the yellowish-white emission from ZnO/SnO2.

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

1. Introduction

Silicon-based light source represents a new path towards integrated, compact and mass manufacturable microsystems for advanced computing, networking, and sensing [1–3]. Silicon light emitting diodes (LEDs) have been demonstrated in the visible spectrum, using porous silicon [1] and most recently, multi-color emission from silicon nanowire [2]. It has also been demonstrated that silicon can be used as a lasing material for optoelectronic integration with existing complementary metal oxide semiconductor (CMOS) circuitry [3]. Integrated optical emitters also play a key role in silicon-based micrototal analysis systems for sensing and imaging [4]. New frontier of biological applications has also been demonstrated. Dislocation-based silicon light emitters, with emission wavelength 1.5 μm, have been used for manipulation of biomolecules [5]. Nanoelectronic light emitting devices [6, 7] incorporating silicon nanowires are emerging as highly sensitive, and real-time detectors of genes, mRNAs, and proteins. We recently demonstrated a nano-scale light emitting diode (LED) created at the silicon probe tip [8, 9], with the potential of near-field scanning optical imaging of nanodrug carrier distributions in biomaterials.

Several techniques have been proposed for silicon-based LEDs. Some have been developed on bulk substrate using ion implantation at high doses typically followed by high-temperature annealing [10]. Others have been demonstrated, using porous silicon [1], silicon/silicon dioxide superlattice [12] and embedding silicon nanoparticles in silicon dioxide [13]. However, silicon, being an indirect band gap material, is fundamentally a poor light emitter [11].
Colloidal quantum dots, due to their unique tunable luminescence properties, have recently been studied as lumophores in light emitting devices on indium tin oxide (ITO) substrates [14–16]. Nanoparticle based light emitting structures with integrated organic layers have shown improved external quantum efficiencies [17]. Despite their high quantum efficiencies, these organic structure are susceptible to atmospheric conditions, moisture, thermal and electrochemical degradation [18–20]. It is hence desirable to have inorganic transport layers for robust LED structures compatible with existing electronics and sensors. Early work on inorganic LEDs had quantum dots sandwiched between either silver and ITO [21] or NiO and ZnO:SnO2 [22]. These LEDs have been developed on ITO substrates, which are not efficient in injecting holes to polymer layers, and an additional hole transporting layers is typically required.

In this paper, we introduce a technique for patterning inorganic QD-based light emitting devices (QD-LEDs), through microcontact printing [23–25] of quantum dots on p-type silicon substrates under room temperature. P-type silicon in the QD-LED structure acts as the hole transport layer, since a p-type silicon anode with a thin layer of silicon dioxide energy barrier can enhance hole injection when compared to ITO as an anode in organic light emitting diodes [26]. The compatibility of microcontact printing with most of the existing silicon microfabrication techniques ensures the future opportunities of the QD-LED on silicon. In addition, microcontact printing is potentially capable of patterning a few number of colloidal QDs with well-defined geometry. We have recently demonstrated controlled deposition of single molecular order of colloidal QDs [27]. Stamping-based microfabrication of a stable light emitting device will have a wide range of applications ranging from integrated circuits (ICs) compatible nanophotonics, microelectromechanical systems (MEMS), to micrototal analysis systems for biomedical research, and to future molecular electronics.

2. Structure design and energy band diagram

The structure of QD-based LEDs consists of multi-layers of inorganic materials: the combination of Au (thickness: 5 nm) and Ag (12 nm) as the cathode, ZnO:SnO2 (ratio 3:1, 40 nm) as the electron transporting layer, CdSe/ZnS particles as the light emission layer, 1nm silicon dioxide and p-type silicon as the bottom electrode. Resistivity of p-type silicon is 10–100 Ω cm. The emission is observed through the top metal cathode, similar to a top emitting organic light emitting diode (TEOLED). Figure 1 gives the structure and the energy band diagram of the inorganic light emitting diode, where the holes are injected from the p-type silicon via silicon dioxide, and transported to the QDs. Similarly the electrons are injected from the Ag/Au negative electrode into ZnO:SnO2 and transported to the QDs. The electron affinity and ionization energy for CdSe QDs are taken from previous experimental data [28, 29].

There are a number of advantages using p-type silicon as a hole injection layer, as compared to ITO [26]. ITO is inefficient in injecting holes to polymer layers whereby an additional hole transporting layers is required before an emitting layer in the system [30–32]. Carrier injection from silicon electrode is improved because most of the electric field drop occurs across the highly resistive layer of thin SiO2. The SiO2 on silicon acts as a buffer layer for the system. The buffer layer will restrain the injected hole current and then improve the balance between hole and electron injection. Resulting high probability of radiative recombination consequently promote luminance and electroluminescence (EL) efficiency [33]. The Fermi level of the silicon is aligned to that of the electroluminescent material [34].

The excitons produced at QD layers can be easily quenched in close proximity to a metal electrode [35]. The ZnO:SnO2 layer hence separates the electroluminescent QD layer from the metal layer where by increasing the radiative recombination. ZnO:SnO2 layer improves the electron injection into the system and simultaneously acts as a hole blocking layer. Band diagram of this device reveals that the barrier injection from ZnO layer into the emitting quantum dots is small. A strong hole injection is offered by the thin SiO2 layer on p-type silicon anode.

3. Fabrication

3.1. Fabrication process

Figure 2 shows the fabrication process. Patterned polydimethylsiloxane (PDMS) stamps were used to stamp
CdSe/ZnS QDs onto bare (100) p-type silicon with 1 nm thick oxide. QDs for the stamping process was prepared as following [23, 24]: first, CdSe/ZnS QDs were precipitated and re-suspended in hexane to remove excess ligands. A hydrophobic colloidal suspension of 15 μl of CdSe/ZnS core shell particles (Evident Technologies) in a 50:50 (v/v) solvent of 1,2-dichloroethane (Sigma Aldrich) and hexane (Sigma Aldrich) making a total of 400 μl solution was prepared. This solution was then pipetted onto a 20 mm diameter convex water surface pinned at the edge by a teflon disk (20 mm inner diameter, 2 mm thick) on a Petri dish. The solvent present on the surface of water evaporates, forming a uniform array of self-assembled nanoparticles due to capillary immersion and convective forces. The film was then picked up by hydrophobic PDMS stamps with circular patterns (diameter: 100 μm) and deposited onto a substrate. This procedure was repeated with QDs with average diameters ranging from 8.4 nm, 9.0 nm, 9.8 nm, with corresponding photoluminescence peaks from 576 nm, 598 nm, 618 nm. The PDMS stamp was fabricated based on the rapid prototyping technique. SU8 photoresist (Microchem Corp.) is patterned photolithographically on a silicon wafer. Depending on the stamp height specification for our device, SU8-2100 (~100 μm thickness) was used. Photolithography process specifications are provided by Microchem Corporation [36]. PDMS (Sylgard 184, Dow Corning Corp.) is then poured over the SU8 master mold, cured at 70 °C for ~30 min, and peeled off the mold to form the microstructures [37]. The PDMS stamps were treated with buffered oxide etchant (ammonium fluoride solution with HF in a 6:1 ratio) for 1 min to prevent sticking onto the substrate during microcontact printing [34]. After stamping, the substrate was annealed at 140 °C for 15 min to remove excess organic solvents [38]. Besides organic materials, inorganic materials have been considered as a transport layer in organic or QD-LEDs. Inorganic materials enhance the stability of solution processed LEDs. MoS 2 [39] and NiO [40] have been used as hole transport layers in OLEDs or QD-LEDs respectively. Some recent publication reports also indicate the use of TiO 2 [41, 42] and ZnO [22, 43] as an electron transport layer in light emitting diodes. Here, a thin film mixture of ZnO:SnO 2, of 40 nm thickness, was RF co-sputtered with a low deposition rate of 0.2 Å s⁻¹ to avoid damage to the QD layer. Sputtered ZnO:SnO 2 without additional oxygen exposure during sputtering acts as an electron transport layer. A transparent top electrode with 120 Å of silver (Ag) and 50 Å of gold (Au) was e-beam evaporated at 0.4 Å s⁻¹ and 0.5 Å s⁻¹ respectively. Optical transparencies of ZnO:SnO 2 films was measured to be 90% (figure 3). Depositing a thin transparent metal Au(5 nm)/Ag(12 nm) electrode reduces optical transmission to 60–40% between 500 and 700 nm emission wavelength, compared to using the ZnO:SnO 2 electrode.

3.2. Nanoparticle thin film characterization

Patterned CdSe/ZnS QDs were deposited onto transmission electron microscopy (TEM) grids with the above described procedure. Figure 4 shows the TEM image of the circular-patterned (diameter 100 μm) particles with a 9.0 nm average diameter (emission wavelength: 598 nm). Well-defined area of packed QDs was observed, roughly suggesting the layer thickness to be a few monolayers. Similar characteristics were observed for particles with diameter 8.4, 9.0 and 9.8 nm.

Thicknesses of deposited particles were further assessed by atomic force microscopy (AFM). An example is shown in figure 5. Particles with emission wavelength 576 nm and particle 8.4 nm were deposited onto silicon and AFM measurement was performed. Peak to peak roughness of the stamped film was less than ~10 nm indicating controlled deposition of the nanoparticle film. The measured thickness of the film was 33 nm indicating deposition of ~4 ML of particles. Thickness measurements using Atomic Force Microscopy (AFM) were correlated with photoluminescence intensity data extracted from the optical micrographs. After measuring the thickness of the film stamped on silicon

![Figure 2. Fabrication process for quantum dot light emitting diode](image)

(a) (100) p-type wafer with 1 nm silicon dioxide grown on surface. (b) Self-assembled quantum dot film was transferred onto a PDMS micropattern. (c) Transfer of quantum dot pattern onto silicon substrate. (d) Sputtering of 40 nm of ZnO/SnO 2 onto the quantum dot substrate. (e) E-beam evaporation of 5 nm of gold and 12 nm of silver.

![Figure 3. Optical transmittance spectrum of top inorganic layers](image)

Solid line: ZnO:SnO 2 (40 nm), Dashed line Au(5 nm)/Ag(12 nm)/ZnO:SnO 2 (40 nm).
Figure 4. TEM images of stamped particles (9.0 nm average diameter) deposited using the microcontact printing technique (the arrows indicate the close-in view into the rectangular window).

Figure 5. Patterned particles with 576 nm emission wavelength: (a) fluorescence image, (b) AFM image indicating the height of deposition 33 nm. (c) Thickness of film measured by the AFM was plotted versus processed fluorescence intensity values. Using the graph plotted thickness distribution of the quantum dot layer can be easily estimated from the fluorescence image without rather time taking AFM measurement. Positive linear correlations were seen in the films with all emission wavelengths tested.

substrates (100 μm diameter stamps), the same sample was imaged under the fluorescence microscope. Fluorescence optical micrograph was processed via MATLAB®, by adding all red green blue (RGB) values per pixel to yield intensity values. Intensity values were obtained at five different points on each same stamped pattern and averaged. This
Figure 6. Photo/electroluminescence from an identical circular pattern (circle diameter: 100 μm). (a) Photoluminescence image. (b) Electroluminescence observed from thinner portion of quantum dot layer. (c) Intensity plot of photoluminescence to estimate local thickness distribution.

was repeated for patterns with different particle thickness. Stamped films exhibited uniformity and evenness throughout each layer; it was assumed that the edge height measured with the AFM corresponded to the film thickness throughout the layer. As shown in figure 5(c), a strong positive, linear correlation between QD film thickness and photoluminescence was observed. As film thickness increases, the fluorescence intensity also increases. Increase in intensity was observed for change in thickness as small as of ~10 nm. Deviations from this correlation can be attributed to the differences in the film density. These measurements indicated that the thickness of QDs varied from one monolayer to ten monolayers, depending on the amount of nanoparticles added to the colloidal suspension as well as the size of the particles used. Therefore, thickness distribution of the quantum dot layer can be estimated using the fluorescence images through the calibration curves shown in figure 5(c).

4. Results and discussion

4.1. Device optimization: monolayer thickness, materials and photoluminescence

The quantum dot thickness plays an important role in device functioning. Figure 6(a) shows the photoluminescence from a circular pattern of 9.8 nm particles deposited with some local thickness variation. Thickness distribution of the quantum dot layer was estimated using the fluorescence image. The RGB image of the photoluminescence was processed using MATLAB® to yield intensity values in figure 6(c). This was correlated to the thickness values shown in figure 5. It was observed that left side of the circle was thinner (20 nm) compared to the right half (50 nm). On application of voltage across the system light emission was observed on the left side of the circle (figure 6(b)). For figure 6(b), driving voltage of 6 V was applied to observe electroluminescence from the left side of the device. Thicker quantum dot layer would result in an increase in operating voltage and decrease of carrier injection [28, 44–46]. The presented technique allows the creation of CdSe/ZnS quantum dot thin film based LED with well-defined geometry and multi-color emission. The relative small non-uniformity of particle distribution is mainly attributed to two factors: (1) CdSe/ZnS nanoparticles are not perfectly spherical in shape, as shown in figure 4 TEMs. Therefore, they tend to cause a minor variation or cracks in the resulting thin film, which causes a non-uniformity in the transfer of particles to the stamp. (2) During the manual operation of the stamps in picking up the film, PDMS stamps may attract small water droplets, which can cause variations in particle density. Due to the surface tension, water droplets tend to distribute quantum dots around its spherical surface. During the evaporation, the particles attached to the spherical surfaces interact and form multi-layers. To further improve the homogeneity of the deposited film, highly localized and controlled version of microcontact printing is under development.

For QD-LED with organic transporting layers, a thickness of 2 ML (for particle size 9.8 nm) was reported to be optimal thickness for light emission [42]. In our case, it was observed that a thickness of 30 ± 5 nm (~3 ML), 40 ± 5 nm (~4 ML), 55 ± 5 nm (~6 ML) is sufficient for good light emission from particles of size 9.8 nm, 9.0 nm and 8.4 nm respectively. Carrier charge into smaller quantum dots has been shown to exhibit lower efficiency than that of larger quantum dots of the same composition. This is due to the mismatch between the highest occupied molecular orbitals (HOMOs) of the QDs and hole transport layers (HTLs).
The quality of the quantum dots on the PDMS substrate depends on the film that is prepared on the convex surface of the water trough. The convex water level curvature was varied by controlling the volume of water used. After a series of experiments, we determined the optimum water level that was used consistently throughout the experiment. The radius of curvature of the convex water surface was optically determined to be approximately around 40 mm. The film was formed after ∼15 min of evaporation. PDMS stamps, with an approximate total area of 25 mm², were used to deposit film.

Mixture ratio of the sputtered ZnO and SnO₂ was further optimized in our silicon inorganic light emitting diodes. Sn acts as an n-type dopant for ZnO. Figure 7 indicates the impact of the emission from ZnO:SnO₂ on the QD EL spectrum for one set of light emitting devices. For a lower driving voltage, the spectrum is dominated by QD emission. As the voltage increases further, ZnO/SnO₂ emission was simultaneously observed along with particle emission. A broad emission was observed from ZnO/SnO₂. The inset image shows the orange light emission (598 nm) from particles and yellowish-white emission from ZnO/SnO₂. This is due to the imbalance between the electron and hole injection at the nanoparticle layer. This reduces the exciton density at the QD layer thereby reducing the emission intensity from particles. The mixture ratio of ZnO and SnO₂ was precisely controlled to obtain proper hole–electron recombination at the QD layer. Emission from ZnO/SnO₂ is typically observed at voltages on the order of 30–50 V. Typical mixture ratio was maintained to be 40% Zn and 25% Sn to reduce operating voltage and thus avoid ZnO/SnO₂ emission.

Concentration of mixture was determined using energy dispersive x-ray (EDX) as shown in figure 8, where 40% Zn and 25% Sn was present. From the TEM image of the deposited film, white portions indicate presence of ZnO and dark areas indicate presence of SnO₂. The size of the ZnO particles in the mixture of ZnO:SnO₂ is comparable to that of the CdSe/ZnS particles used in the system.

4.2. Electroluminescence measurement

With modest turn on voltage, electroluminescence is observed at room temperature. Most of the diodes demonstrated steady light emission for more than an hour of operation, proving the great stability of inorganic multi-layer structure. Electroluminescence from QD-LEDs with different average QD diameters is shown in figure 9. Emission from circular-patterned particles of size 7.8 and 9.8 nm was observed. Figures 9(a)–(d) are for particles of size 9.8 nm (photoluminescence peak: 618 nm) and 7.8 nm (564 nm), respectively. For the electroluminescence in figure 9(d), one can observe slight emission of ZnO/SnO₂ mixture along with...
particle emission. A larger voltage was required to view light emission from smaller particles as 7.8 nm, resulting in simultaneous emission from ZnO/SnO$_2$ on the background.

Figure 10 shows the basic characteristics of the QD-LEDs with three different colors. Electroluminescence spectrum and image of the working device were observed indicating that the emission from the device is dominated by the emission from the quantum dots layer. Current–voltage characteristics are shown in figures 10(a1)–(c1). Forward bias is observed when p-type silicon is the positive electrode and Ag/Au electrode is grounded. Turn on voltages for LEDs with average particle size 9.8 nm, 9.0 nm and 8.4 nm were 2 V, 4 V and 5 V respectively. It was observed that for all the devices forward current increases as the forward voltage increases. Smaller the particle, larger is the band gap and so is the required turn on voltage for the device to show light emission. It was observed that the current required to view light emission was on the order of 40–50 μA mm$^{-2}$. Current–intensity plots in figures 10(a2)–(c2) indicate a linear relationship between the increase in intensity and current flow through the device.

In literature it has been reported that luminance of 53 cd m$^{-2}$ at a current density 860 μA mm$^{-2}$ and at a voltage 14 V was observed for TOLED with Si anode [47]. In this paper the luminance of the device at 10 V with CdSe/ZnS nanoparticles, of particle size 9.8, 9.0 and 8.4 nm was observed to be 482, 375 and 489 cd m$^{-2}$ for emission wavelength 622.
598 and 576 nm was calculated for the particular emission area. The current density of 147 μA mm\(^{-2}\), 120 μA mm\(^{-2}\) and 375 μA mm\(^{-2}\) was measured for 1 mm × 1 mm top electrode dimension for diodes with nanoparticles of size 9.8 nm, 9.0 nm and 8.4 nm respectively.

Figures 10(a3)–(c3) show the electroluminescence and photoluminescence of the LEDs plotted for particle size 9.8 nm, 9.0 nm and 8.4 nm, respectively. A strong electroluminescence band was observed from CdSe particles with full width half maximum (FWHM) of ~40 nm. This was observed to be similar to that of photoluminescence. The electroluminescence emission peak was observed at 622 nm, 598 nm and 576 nm for the red, orange and yellow emitting devices, respectively. A slight red shift was observed between the photoluminescence (peaked at 618 nm) and electroluminescence (622 nm) spectra in figure 10(a3). This is similar to the CdTe particles that have a red shift due to the trap filling or detrapping on the surface states [48]. The small red shift of (~5 nm) and slight broadening of the electroluminescent spectra, when compared to the photoluminescence spectra, can also be attributed to effects such as energy and charge transfer among nanoparticles [29, 49]. It was also observed that the power consumed by these devices was typically small. For instance, devices with 9.8 nm particles consumed typically 5 mW power for an area of 1 mm × 1 mm.

5. Conclusion

We fabricated quantum dot based inorganic light emitting diodes through stamping nanoparticles directly onto silicon hole transporting layer. The creation of quantum dot monolayer can be done at room temperature using microcontact printing via PDMS. The generation of excitons in the quantum dot layer occurs through direct charge injection. Electrons are injected from Ag/Au contact through the ZnO:SnO\(_2\). They are eventually transported to the QDs where they are better confined due to their higher electron affinity. Optimal thickness of monolayers of nanoparticles stamped onto to the substrate was determined by atomic force microscopy (AFM). Thickness of the nanoparticle film varied between 30 nm, 40 nm and 50 nm (±5 nm) depending on the size particles 9.8 nm, 9.0 nm and 8.4 nm respectively were found optimal for our silicon-based QD-LED. When voltage was applied to the QD-LED, electroluminescence (peaked at 622, 598 and 576 nm) identical to the photoluminescence (618, 598 and 576 nm) was observed depending on the average diameter of the used QDs (9.8 nm, 9.0 nm and 8.4 nm, respectively). The LED demonstrated steady light emission for hours of operation, proving the great stability of inorganic multilayer structure. The ease of fabrication and processing of colloidal QD on silicon, through microcontact printing and further integration with metal oxides, open up the possibilities for creating nanophotonic microsystems with mass reproducibility and enable robust, compact and tunable imaging, sensing and display applications.

Acknowledgments

This research was performed in part at the Microelectronics Research Center (MRC) at UT Austin, the National Nanotechnology Infrastructure Network (NNIN) supported by the National Science Foundation (NSF NNIN-0335765), and the Center for Nano and Molecular Science and Technology (CNM) at UT Austin. We thank NSF EPDT Program (ECS-26112892), NSF IMR Program (DMR-0817541), UT Research Grant, the Welch Foundation, and The Strategic Partnership for Research in Nanotechnology (SPRING) for partial financial support of this work.

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