Surface Engineering of Silicon Quantum Dots: Does the Ligand Length Impact the Optoelectronic Properties of Light-Emitting Diodes?

Josef Mock,* Elisabeth Groß, Marc Julian Kloberg, Bernhard Rieger, and Markus Becherer*

Herein, silicon quantum dot light-emitting diodes (SiQD LEDs) are investigated to explore the interplay between their electroluminescence (EL) blue shift and the SiQD ligand length on the SiQD surface. The ligand is essential for LED fabrication to ensure colloidal stability, but it also hinders efficient charge transport inside the LED. Consequently, the SiQDs are functionalized via organolithium reagents with hexyl, octyl, and dodecyl to obtain a low-SiQD surface coverage and therefore improved charge transport. With increasing ligand length, the potential barrier between the SiQDs increases, which is ideal for charge carrier confinement, but a trade-off with the charge transport has to be found. A sweet spot for LED performance is found for octyl-functionalized SiQDs with the highest irradiance (734 μW cm⁻²) and external quantum efficiency (1.48%), compared with shorter hexyl- and longer dodecyl-capped SiQDs. The SiQDs exhibit a size distribution, whereas the bandgap energy of SiQDs is inversely proportional to the SiQD size. Therefore, large SiQDs with a short ligand are accessible at low voltages, whereas small SiQDs with long ligands require elevated voltages. This leads to a broadening and a blue shift of the EL spectrum and a ligand length-controlled size-selective SiQD activation.

1. Introduction

Organic light-emitting diodes (OLEDs) have been omnipresent for many years but they still suffer from faster degradation compared with inorganic LED technology. To tackle this problem, research has been driven toward luminescent semiconducting nanocrystals, also called quantum dots (QDs), as the active material. These QD LEDs (QLED) combine the advantages of OLEDs, such as solution processibility, with the bright and stable emission of inorganic QDs. However, many QLEDs use rare or toxic group II–VI and III–V materials. Instead, silicon is a nontoxic, Earth-abundant material and the backbone in electronic chip fabrication, which can step in for common QDs. When silicon crystallites reach sizes below their exciton Bohr radius (<4.5 nm), they start to show photoluminescence (PL) due to the quantum confinement effect. This effect has been studied in numerous silicon nanostructures, such as porous silicon, Si wires, 2D Si sheets, and Si QDs (SiQDs). Especially SiQDs have gained significant attention in numerous research fields, such as solar cells, nonlinear optics, sensors, biomedical applications, field-effect transistors, and LEDs. Suitable SiQDs for LED fabrication are commonly synthesized via bottom–up and top–down approaches, namely, plasma synthesis and solid-state etching from SiO₂ matrices. In LEDs, SiQDs are usually embedded in a hybrid multilayer OLED structure and act as the active emitting material. High-efficiency SiQD LEDs have been demonstrated with external quantum efficiencies (EQE) of up to 8.6%. Furthermore, multicolor LEDs were fabricated, showing the diversity of SiQD-based LED technology by changing the SiQD size. Those promising examples show that SiQDs can be a versatile and nontoxic alternative to existing QDs for LEDs.

In pursuit of SiQD LED research, the role of surface ligands, as an essential part of SiQDs, has not gained enough attention. For SiQDs, ligands play a substantial role as capping agents in synthesis by tuning their emissive color or increasing the long-term stability. For the fabrication of SiQD LEDs, the surface ligand ensures the essential colloidal stability. The conventional method to functionalize SiQDs relies on the hydrosilylation (HS) reaction, where the H-terminated SiQD surface is fully functionalized with an unsaturated...
Many ligands are insulating hydrocarbons that provide the necessary colloidal stability but also hinder efficient charge transport. As the removal of the surface ligands in the deposited films is difficult to achieve, a way to exploit and improve the ligand shell is necessary.\cite{23,38,40} In SiQD LEDs, electric charge transfer in the QD layer was improved by a ligand with conjugated π–π structures instead of alkyl chains, but the used octyl-ligand showed an overall better LED performance.\cite{43}

Not only the type of ligand has an influence on the performance of Si QLED but also the used functionalization method. It was found that the functionalization with organolithium reagents (OLR) leads to less overall surface coverage in contrast to HS, which results in a denser film packing and therefore a higher conductivity.\cite{25,44} Functionalized by HS or OLR, many SiQD LEDs exhibit a blue shift of the electroluminescence (EL) spectra with increasing voltages.\cite{25,29} Because the bandgap is inversely proportional to the SiQD size and ensembles of SiQDs always exhibit minor differences in size, higher-bandgap QDs (i.e., smaller size) only become accessible as the voltage increases.

While the EL shift with the driving voltage is a well-known phenomenon for SiQD LEDs, an analysis of the SiQD size distribution in combination with the surface ligand remains absent in literature. Furthermore, the ligand’s influence on the electric LED characteristics is well known, but no report has systematically shown the effect of different alkyl ligands. We combine both and present a systematic study on the influence of alkyl ligand length on the electrical and optical characteristics in SiQD LEDs. This combination allows us to bring more insight into the interplay between the LED current density–voltage (J–V) characteristic, the EQE, the emission color, and the ligand length. Therefore, SiQDs functionalized with hexyl, octyl, and dodecyl organic ligands were synthesized via the OLR method to start with an already improved charge transfer, due to the overall lower conductivity. As the removal of the surface ligands in the charge transport in the multilayer LED structure is discussed by investigating the J–V characteristic. Measuring the EL spectrum at every voltage step allows us to extract the irradiance and, together with the current density, the EQE. The EL spectra further allow us to investigate the color stability of the produced SiQD LEDs by tracking the intensity, the peak position, and the full width at half maximum (FWHM) of the optical LED emission.

2. Results and Discussion

2.1. Synthesis and Characterization of SiQDs

In this article, all SiQDs are synthesized from hydrogen silsequioxane (HSQ) according to the method proposed by Hessel et al.\cite{45} and shown in Figure 1a. The SiQDs are passivated using the OLR method developed by Höhlein et al.\cite{44} for improved charge transport within the later-fabricated LEDs.\cite{23} OLR results in a lower surface ligand coverage because only every second H bond is functionalized. The reaction mechanism in Figure 1b shows that a theoretical maximum of 50% surface coverage is possible. N-alkyl lithium reagents with 6, 8, and 12 carbon atoms are applied as surface groups on the SiQDs.

The diameter of the SiQDs was determined by transmission electron microscopy (TEM) to be 3.5 ± 0.67 nm. An exemplarily image of SiQD-Hex and the corresponding histogram is shown in Figure 2. The SiQD size matches with the size-dependent PL emission maximum of ≈710 nm, as reported by other research groups.\cite{46,47} In addition, the theoretical model of Park et al. shows that the SiQD size is consistent with the bandgap emission.\cite{48}

The Fourier-transform infrared (FTIR) spectra in Figure 3a confirm the successful functionalization of all three SiQD compounds. The strong C–H stretching bands (µ(CHx)) at 2800 cm⁻¹ as well as the deformation bands (δ(CHx)) at 1400 cm⁻¹ indicate the presence of alkyl side chains. Only minor oxidation at 1050 cm⁻¹ (Si–O stretching) is observed for all samples. The relative intensity of the Si–H stretching band (2100 cm⁻¹) decreases from hexyl to dodecyl due to longer chain lengths.

Figure 3c shows thermal gravimetric analysis (TGA) of surface-capped SiQDs. For all three samples, the removal of the organic ligands is observed between 300 and 400°C. SiQD-Hex and SiQD-Oct show a relative mass loss of ≈25%, whereas SiQD-Dodec loses 41%. The surface coverage is determined by a combination of these results with the computational model by Avarmov et al.\cite{49} (Supporting Information). SiQD-Hex and SiQD-Dodec exhibit a surface coverage slightly above 40%. The lowest surface coverage of 33% is determined for SiQD-Oct. These results are lower than the aforementioned theoretical maximum surface coverage of 50% due to steric hindrance.\cite{50}

Besides confirming the successful passivation, investigation on the optical properties of SiQDs is important for the implementation in QD LEDs. A photograph of the red PL of
SiQDs-Hex in toluene is shown in Figure 3b and confirms that the colloidal stability is ensured even with a surface coverage below 50%. The PL spectra of the three SiQDs in Figure 3d show a peak emission maximum at \( \approx 710 \text{ nm} \) with a FWHM of 140 nm for all three samples. In the case of alkyl-capped SiQDs, the mechanism of bandgap emission dominates.\(^{35}\)

The UV/VIS absorption spectra in Figure 3d show the SiQD absorption normalized to the signal strength of 300 nm for all three ligands. The absence of other absorption bands indicates that the samples are free of unsaturated substances or side products.

2.2. SiQD LED Fabrication and Morphology Characterization

After confirming similar quality SiQDs, LEDs with each functionalization were fabricated. This section discusses the
fabrication quality of the SiQD LEDs. The true influence of the ligand length on the LED performances is only observed if the SiQD LEDs are comparable. A SiQD LED mostly consists of spin-coated layers and is schematically shown in Figure 4a. A thickness profile of each layer is shown in Figure S1, Supporting Information. The indium tin oxide (ITO) layer serves as the device anode on which the hole-injection layer poly(3,4-ethylene-dioxythiophene) polystyrene sulfonate (PEDOT:PSS) is deposited to facilitate good hole injection for the LED. The hole-transport layer poly(4-butylphenyldiphenylamine) (poly-TPD) reduces the energy step to the next layer for efficient charge transport. Poly-TPD additionally acts as an electron-blocking layer because of its high lowest unoccupied molecule orbital (LUMO) level. The SiQD layer is the emissive layer, where the charge carriers (CC) radiatively recombine. The zinc oxide (ZnO) hole-blocking layer also eases the electron injection from the top Ag cathode. Furthermore, Ag acts as a mirror for backward emitted photons.

Figure 4a shows the suggested energy diagram for the SiQD LED. One can see that a sufficient blocking of holes (2 eV) and electrons (1.5 eV) exists and small barriers of maximum 0.5 eV enable the CC transport. All energy levels are taken either directly from the manufacturer or literature [25,30,51]. The fabrication of the SiQD LEDs is conducted by spin coating, which is a well-developed technique to manufacture thin films with little deviation in thickness. However, as the SiQD LEDs are not processed under cleanroom conditions, small but macroscopic defects (pinholes, particles, etc.) in the 3 × 3 mm large devices can occur.[52] Microscope images of the EL of a defect-free SiQD LED (left) and a SiQD LED with defects in the micrometer range (right) are shown in Figure 3c. The quality of some LED stacks is additionally checked by atomic force microscopy (AFM) to reveal defects on the nanometer scale and is exemplarily shown in Figure S2, Supporting Information. It shows the full LED stack of ITO/PEDOT:PSS/poly-TPD/SiQD/ZnO with a low surface roughness below 2 nm and an agglomerate (~15 nm height and 400 nm diameter). This measurement shows that besides the defects on the micrometer scale, only few defects on the nanometer scale are present. They can occur, for example, from polymer agglomeration, spin-coating defects, or particles. For efficient LEDs, the transport layers have to show as high as possible transparencies as the outcoupling efficiency ηout limits the EQE.[53] Therefore, in Figure 3d, transmission spectra are given for each transport layer. Each layer shows a transmittance (> 89%) for wavelengths increasing from 450 nm. This high transparency matches well with the SiQD emission above 500 nm, as shown in Figure 2d; thus, the overall LED performance is not affected by absorption of other materials.

2.3. SiQD LED Electro-Optical Characterization

To study the influence of the ligand, first, the electrical and second the optical properties of the fabricated SiQD LEDs are analyzed and discussed. To account for variations, 13 SiQD-Hex, 7 SiQD-Oct, and 5 SiQD-Dodec LEDs with small or no defects were analyzed. In Figure 5a, the absolute values of J are plotted in a log scale against the applied voltage, ranging from ~3 to 6 V. The J–V characteristics for one type of LED spread over one order of magnitude at a single voltage. This variation indicates that only small defects or inhomogeneities in the layers affect the LED characteristics to a certain degree. In the reverse diode direction, J is mainly influenced by pinholes and other defects inside each LED.[52,54] In the forward direction, a clear current onset at around 2 V can be detected for SiQD-Hex and SiQD-Oct LEDs. SiQD-Dodec LEDs only reach ~3.5 mAcm⁻² at a voltage of 14 V, whereas both other functionalizations exhibit several hundred
mA cm$^{-2}$ at 6 V. The surface ligand acts as a small tunneling barrier between the SiQDs and scales with the ligand length $l$ and therefore attenuates the current through the device.\cite{38,55}

Figure 5d schematically shows the intra-QD distance $d$ of two SiQDs together with the barrier in the band diagram. With increasing $l$, $d$ widens and the carrier mobility deteriorates.\cite{56}

For densely packed films we calculated the lengths of our SiQD-to-SiQD distances to be 1.26, 1.76, and 2.74 nm for SiQD-Hex, SiQD-Oct, and SiQD-Dodec, respectively (Supporting Information). During device operation, additional space charges are induced and lead to a space-charge-limited current (SCLC) in the device.\cite{57}

Figure 5e shows the effect of SCLC on the carrier transport in a SiQD layer without (left) and with SCLC (right). The uneven tunneling barrier can cause an imbalance of CCs in the SiQDs, affecting the recombination rates. The EQE in Figure 5c shows the calculated EQE for all SiQD-LED devices (See Equation S6, Supporting Information). We see that the mean EQE is $\approx$1% for most LEDs but reaches maximum values of 1.33% for Hex, 1.48% for Oct, and 0.92% for Dodec QDs. With increasing $J$, the EQE decreases. The radiative recombination is enhanced by optimized CC confinement in the SiQDs with an octyl ligand. Dodec LEDs have the lowest EQE of all compared devices.

Figure 5. a) $J$–$V$ characteristic of all LEDs showing the typical asymmetric diode behavior. The legend also applies to (b) and (c). b) Irradiance against $V$, reaching maximum irradiance values of 628 $\mu$W cm$^{-2}$ for Hex, 734 $\mu$W cm$^{-2}$ for Oct., and 25 $\mu$W cm$^{-2}$ for Dodec-functionalized LEDs. c) EQEs, reaching maximum values of 1.33% for Hex, 1.48% for Oct, and 0.92% for Dodec QDs. With increasing $J$, the EQE decreases. d) Schematic illustration of two SiQDs next to each other. The actual SiQD is gray, whereas the blue shell represents the organic ligand with length $l$. The band structure with the barrier is sketched.

To compare the optical output of the SiQD-LEDs, the irradiance is plotted against voltage, as shown in Figure 5b. We defined a high turn-on irradiance of 10 $\mu$W cm$^{-2}$, where the LED can be seen as ON with bare eyes. For clarification purposes, all data points below turn-on are removed to directly see the turn-on voltage, $V_T$, of 2, 2.5, and 9 V for SiQD-Hex, SiQD-Oct, and SiQD-Dodec LEDs, respectively. For Hex and Oct LEDs, $V_T$ is still comparable with SiQD-LED structures that define $<100$ nW cm$^{-2}$ turn-on irradiances, which is not visible with bare eyes.\cite{32,43} The maximum irradiances $I_{\text{max}}$ for SiQD-Hex, SiQD-Oct, and SiQD-Dodec LEDs lie at 628, 734, and 25 $\mu$W cm$^{-2}$, respectively. At 5 V, a crossover of the irradiance of Hex and Oct LEDs occurs. From this point onward, the recombination rate for Oct LEDs is higher at high voltages than the rate for Hex LEDs. At high voltages, the CC localization becomes insufficient for Hex LEDs and the irradiance degrades. For Oct LEDs, the CCs are better localized because electron tunneling is dependent on the potential barrier height and width, which is formed by the ligands.\cite{57} Liu et al. found that the potential barrier for electrons is lower than for holes, resulting in a lower tunneling probability for holes than electrons.\cite{58} The uneven tunneling barrier can cause an imbalance of CCs in the SiQDs, affecting the recombination rates.

To counteract the current limitation, conjugated molecule systems with $\pi-\pi$ stacking for enhanced conduction have been implemented.\cite{43,62} Nevertheless, introduced $\pi-\pi$ stacking of allylbenzene can enhance the charge transport but also cause a charge imbalance in the active layer, which ultimately decreases the EQE.\cite{41,43}
So far, we observed an optical power attenuation through the Dodec ligand, whereas the Oct ligand even improved the output. To gain more knowledge, we now investigate the position of the peak emission and the FWHM of the EL spectra of the SiQD LEDs. The EL spectrum is known to shift toward smaller wavelengths with increasing driving voltages, and in Figure 6a, an EL spectrum of a SiQD-Hex LED is exemplarily plotted from $V_T$ until $I_{\text{max}}$. The black arrow indicates the increase in irradiance with the voltage, whereas the red arrow highlights the blue shift $\Delta \lambda$ of the peak emission point of each EL spectrum. The EL shift is commonly attributed to an inhomogeneous size distribution of the SiQDs.\(^{[29,32,62,63]}\) In Figure 6d, a schematic model visualizes the effect of the inhomogeneous size distribution. Large SiQDs exhibit a smaller bandgap than smaller SiQDs. At low driving voltages, not all SiQDs are accessible for the CCs, whereas with increasing driving voltages, the CC can excite smaller-sized SiQDs with larger bandgaps. At the same time, through the activation of a wider SiQD size distribution, the FWHM broadens and the EL spectrum blue shifts. Furthermore, ligands and dangling bonds on the SiQD surface can couple with surrounding phonons and broaden the EL FWHM.\(^{[64]}\) This effect is even stronger when driving LEDs, as an enhanced phonon-concentration is present due to the Joule heating effect,\(^{[65]}\) where the LED current causes elevated temperatures.

The broadening of the EL FWHM is shown in Figure 6b from $V_T$ until $I_{\text{max}}$. At voltages of 2 and 2.5 V, the FWHM of Hex and Oct LEDs starts at $\approx 110$ and 115 nm, respectively. At higher voltages from 9 V on, the Dodec LEDs are turned on and exhibit a higher starting FWHM of $\approx 130$ nm. The FWHM data points increase with increasing voltages and follow the same linear trend. The Dodec LED data show a bigger deviation than the other LEDs due to low intensity and noisy EL spectra. As a result, the EL FWHM of Dodec LEDs reaches maximum value of 150 nm, which is even broader than the PL FWHM of 140 nm. At the point where the EL FWHM reaches the PL value, one can assume that all SiQDs in the emissive layer are reached by the injected CC. For the Dodec LEDs, the mean voltage is $\approx 12$ V, whereas the Hex and Oct LEDs do not reach this point before the irradiance starts to decrease.

In Figure 6c, the peak positions of the EL and PL spectra are compared. Therefore, the value of the EL peak is subtracted from the PL peak and that difference is plotted over the applied voltage. The difference of the EL position to the PL position becomes smaller with increasing $V$ for all three SiQD LED types. At $V_T$, the maximum deviation is 71 nm at 2 V, 56 nm at 2.5 V, and 19 nm at 8.5 V for Hex, Oct, and Dodec LEDs, respectively. All three LED types approach the PL position with the same trend. Hex and Oct LEDs reach minimum values of 12 and 16 nm at 6 V, whereas Dodec LEDs reach the PL value at 12 V. That voltage value matches the voltage where the EL FWHM reaches the PL one. With increasing ligand length and higher applied voltages, the difference of the EL and PL spectrum is minimized. By selecting the right ligand length in this study, we influence the SiQD size which is activated and in turn, the emission color of the fabricated SiQD LEDs. The emission color of Oct LEDs shows only little deviation from Hex LEDs, although they exhibit superior irradiance and EQE compared with the other fabricated LEDs.

3. Conclusion

A systematic study of hybrid SiQD LEDs with three alkyl ligands, hexyl, octyl, and dodecyl, is presented to investigate their influence on the electrical and optical characteristics. The SiQDs are functionalized with the OLR method that enables a low SiQD surface coverage below 50%, while still providing sufficient

Figure 6. a) EL spectrum of a Hex LED from $V_T$ until $I_{\text{max}}$. The black arrow shows the irradiance increase with the voltage and the red arrow indicates the blue shift of the peak. b) FWHM over $V$, showing a broadening with increasing voltages. c) The evolution of the difference of EL and PL peak emission in nm from $V_T$ until $I_{\text{max}}$. With increasing voltages, the difference declines toward zero. d) Schematic illustration of the connection between the SiQD size, their bandgap, and the FWHM.
colloidal stability for device fabrication. The three different SiQDs were tested in the same LED configuration. The increase in the ligand length on the SiQDs reduces the LED current density by several orders of magnitude, and $V_{T}$ shifts toward higher voltages. In our measurements, SiQD-Oct not only provides an optimum length because of the highest irradiance and EQE of 734 $\mu$W cm$^{-2}$ and 1.48%, but it is also superior at high $J$ against the other ligand lengths. We assign that to the improved CC confinement in the SiQD layer. The EL spectra undergo a broadening and a blue shift with increasing voltages. For Dodec LEDs, the FWHM broadens to the PL value of 140 nm, whereas the Hex and Oct LEDs do not reach that value. By tracking the EL spectra, we calculated the difference of the blue-shifting EL to the PL peak position. This difference follows the same trend as the spectral FWHM, where Hex and Oct did not reach the PL position, but Dodec did. By the ligand length, we can determine the SiQD size, which can be reached by the CC, thus allowing us to tune the emission color. The presented results show that there is a trade-off between color tuning and high irradiance together with a high EQE. When high-performance SiQD LEDs are required, short ligands such as Hex and Oct are preferred, whereas with the long Dodec ligand, the EL spectrum can be tuned. The combination of color tuning and high-performance SiQD LEDs might be possible in the future with improved LED layouts.

4. Experimental Section

SiQD Synthesis: HSQ was annealed for 1 h at 1000 °C to obtain 3.5 nm small SiQDs embedded in a silica matrix. The SiQDs were liberated by etching with HF and subsequently functionalized with the organometallic reagents hexyl–, octyl–, and dodecylithium, respectively. See the detailed description in Supporting Information.

Characterization of SiQDs: Bright-field TEM images were obtained using a JEOL-2012 electron microscope equipped with LaB6 filament and operated at an accelerating voltage of 200 kV. Particle size distribution was calculated by counting at least 200 particles using ImageJ software (Version 1.49). FTIR measurements were carried out with liquid nitrogen-cooled Bruker Vertex 70 A on an attenuated total reflection module and a resolution of 4 cm$^{-1}$. All spectra were collected by the software Opus and reported in transmission mode. TGA measurements were carried out with freeze-dried samples in aluminum oxide pans inside a glovebox on a Netzsch TG 209 F 1 Libra. The heat rate was 10 °C min$^{-1}$ from 30 to 750 °C under argon flow of 20 mL min$^{-1}$. A calibration of an empty pan was conducted prior measurement. The data were evaluated with the software Netzsch Proteus 6. PL spectroscopy was conducted using an Avantes AvaSpec 2048 × 64TEC spectrometer from Avantes. A two-channel Keithley 2602A source measure unit was used to characterize the LEDs electrically. The measurement was controlled with the software Matlab.

Single-Layer Characterization: The transmittance spectra were measured in the visible range using an AvaLight-DH-S-BAL as the light source and were recorded by an AvaSpec 2048 spectrometer. The spectrometer was calibrated with a glass substrate to determine the pure transmission of each film. Layer thickness measurements were taken on reference films with a Bruker DektakXT. Therefore, the step height across a thin cut in the reference layer was measured. AFM images were recorded using an Asylum Research AFM MFP-3D from Oxford Instruments in tapping mode. All AFM images were analyzed with the software Gwyddion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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