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High power efficiency in Si-nc/SiO$_2$ multilayer light emitting devices by bipolar direct tunneling

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We demonstrate experimentally bipolar (electrons and holes) current injection into silicon nanocrystals in thin nanocrystalline-Si/SiO$_2$ multilayers. These light emitting devices have power efficiency of 0.17% and turn-on voltage of 1.7 V. The high electroluminescence efficiency and low onset voltages are attributed to the radiative recombination of excitons formed by both electron and hole injection into silicon nanocrystals via the direct tunneling mechanism. To confirm the bipolar character, different devices were grown, with and without a thick silicon oxide barrier at the multilayer contact electrodes. A transition from bipolar tunneling to unipolar Fowler–Nordheim tunneling is thus observed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3147164]

Nanocrystalline silicon (Si-nc) is a way to achieve visible light emission from silicon with a good efficiency.[1] To obtain an efficient light emitter, balanced bipolar charge injection into the nanocrystals has to be realized, which is difficult because of the composite nature of the material. There is a trade-off between low Si-content nanocomposites with isolated and well passivated Si nanocrystals, which have high recombination efficiency and high Si-content nanocomposites, where high conduction occurs, which leads to optimized charge injection into the nanocrystals under low voltages. In principle, bipolar injection should be possible when the thickness of the silicon oxide between the nanocrystals is reduced at a value that tunneling currents become important. Direct tunneling is a conduction mechanism that leads to large injected electrical currents at low applied voltages without leading to oxide degradation. Present silicon light emitting devices (LEDs) work under high voltages (above 5 V) at which unipolar field-enhanced Fowler–Nordheim (FN) tunneling is the main charge injection mechanism.[1,2] Under this regime, the charge transport in the oxide takes place via hot electrons and the electron-hole pairs are generated by impact ionization in the Si-nc. Hot electron transport leads to a fast degradation of the oxide matrix and low device endurance. Our research efforts are aimed at the realization of a device that operates at low voltages under balanced bipolar charge injection into nanocrystals.

In this work we will demonstrate bipolar charge injection at low applied electric fields in Si-nc/SiO$_2$ multilayer (ML) LEDs. Electrons and holes are injected through direct tunneling into the Si-nc from cathode and anode, respectively, which is followed by their radiative recombination. LEDs power efficiency at low applied voltages shows the highest value among the reported data for this type of devices.[2] By increasing the applied voltages, FN tunneling of electrons into the conduction band of silicon oxide becomes dominant, power efficiency drops and light emission is due to impact ionization.

The device structure is a metal oxide semiconductor capacitor where alternating stoichiometric SiO$_2$ and silicon-rich oxide (SRO) layers with large Si excess is used as the gate oxide. The nominal thickness of SRO and oxide layer within a ML is 3 and 2 nm, respectively. Silicon nanocrystals were formed by annealing the ML at 1150 °C for 30 min in nitrogen. Si *p*-type substrate was used. Details on fabrication, structural characterization, and experimental procedures could be found elsewhere.[3,4] The gate area of the LED is 1.02×10^{-3} cm^2. Three structures with five ML periods were grown (Fig. 1): W32—the ML with 2-nm-thin oxide at both top (gate) and bottom (substrate) of the ML stack; W32HB—the ML with 2-nm-thick oxide at the top and 4-nm-thick at the bottom of the ML, which serves as a tunneling barrier for holes; W32EB—the ML with 2-nm-thick oxide at the bottom, and 4-nm-thick oxide at the top of the ML which serves as the tunneling barrier for injected electrons.

Figure 2 shows power efficiency as a function of injected current density for W32. The maximum power efficiency of 0.17% is achieved at the smallest injected current density of 4.9×10^{-4} mA/cm^2, where the optical power density is 1.4×10^{-3} μW/cm^2. The applied gate voltage is 1.7 V, which corresponds to an electric field of 1.1 MV/cm. (The applied electric field is calculated as the ratio of the applied gate voltage to the actual ML thickness, which is 15.6 nm for W32, and 17.3 nm for both W32EB and W32HB.) This is the largest power efficiency value at the smallest gate voltages reported so far for this type of electroluminescent

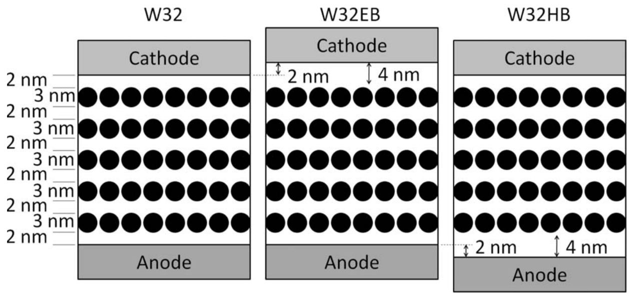

FIG. 1. Schematic cross section of three devices: W32, W32EB, and W32HB. Silicon nanocrystals—black dots and silicon oxide matrix—white background. Note that the overall SiO$_2$ thickness facing the electrodes is 2 nm for W32 and 2 nm or 4 nm for W32EB and W32HB.

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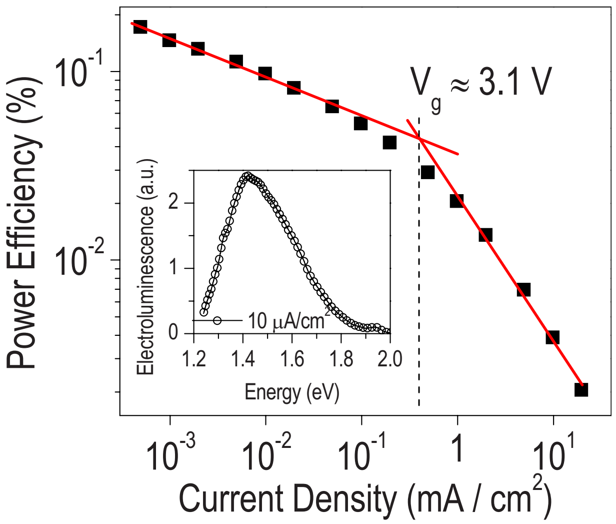

FIG. 2. (Color online) Power efficiency as a function of the injected current density for the ML device without a thick injection barrier (W32). The dashed line indicates the current density which separates dominant bipolar injection, which is more efficient, from dominant unipolar injection through the FN tunneling. The inset shows the electroluminescence spectrum of W32 recorded for an injection current of 10 μA/cm^2. The spectrum is normalized to a spectrograph response.

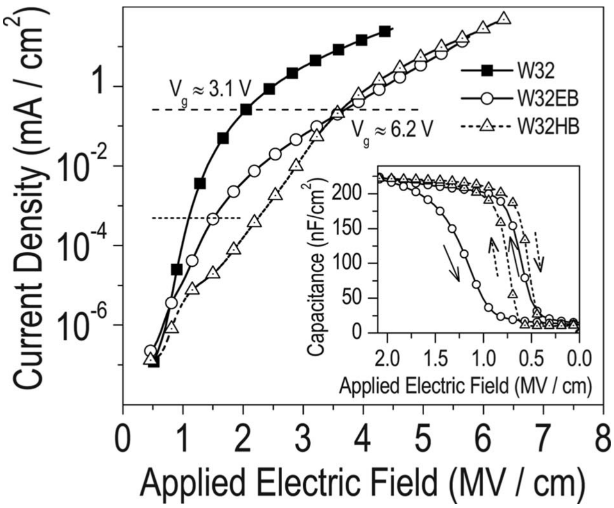

FIG. 3. Current density as a function of the applied electric field (*I-V* characteristics) for three MLs: without thick injection barriers—solid squares, with the electron injection barrier at the gate—open circles and with the hole injection barrier at the substrate—dotted triangles. The dashed line shows the transition current density (Fig. 2). The dotted line shows the onset of EL for W32 and W32EB. Inset shows capacitance-voltage characteristics for W32EB and W32HB devices. Arrows indicate the scanning direction of the hysteresis loop.

devices.[2,4,5] The high power efficiency is attributed to the radiative recombination of excitons formed by both electron and hole injection into silicon nanocrystals via direct tunneling mechanism. The maximum optical power density of 2.6 μW/cm^2 is reached at the largest injected current density of 20 mA/cm^2 when the power efficiency is the smallest, 2×10^{-3}%. The power efficiency dependence on injected current shows two distinct regions: a region of low currents, when the efficiency decreases slowly, and a region of high currents, when it decreases rapidly. The first region is attributed to the bipolar (electrons and holes) injection into silicon nanocrystals under the direct tunneling regime. The direct tunneling is the dominant charge transport mechanism in structures with thin, <2.6 nm, oxide layers.[6,7] The fact that we measure high efficiency shows that direct tunneling is important to achieve high efficiency. The second region of high current densities is due to the dominant unipolar (electron) injection into silicon oxide conduction band by the field-enhanced FN tunneling.[7,8] The transition between these two regions occurs at the applied voltage of 3.1 V (an applied field of 2.0 MV/cm), which corresponds to the energy barrier height (band offset) for electrons at the Si/SiO$_2$ interface. The electron barrier height controls the onset of FN tunneling. In the second region, i.e., above 3.1 V, electrons from the gate are injected in the conduction band of the silicon oxide: these hot electrons loose energy by electron-hole pair generation in Si-nc or by creating defects in the oxide matrix. The power efficiency in the FN regime of our LED is comparable to the one of Ref. 9, which has power efficiency of 5.6×10^{-3}% (external quantum efficiency of 0.2% with an operating voltage of 36 V). This shows that the FN regime yields lower efficiency than the direct tunneling regime.

In order to prove the bipolar character of charge injection at low bias, we studied the electro-optical characteristics of W32HB and W32EB (Fig. 1). The thick oxide layer in W32HB will block injection of holes from the anode (*p*-type Si substrate). Likewise, the thick oxide at the cathode side (*n*-type polycrystalline Si gate) should block the electron injection in W32EB.

Figure 3 shows the *I-V* characteristics for the three devices in forward bias (negative potential is applied on the gate). W32HB shows smaller current densities than W32EB at the low/medium applied electric field, i.e., in the regime of direct tunneling. At higher electric fields when the FN tunneling becomes dominating, the same current densities are achieved. At the same current density, the applied electric field for both W32HB and W32EB is larger than that for W32. This is because of a large voltage drop in the thicker oxide layer, i.e., the barrier. The electric field in the barrier oxide was calculated from the *I-V* curves as the voltage difference between the *I-V* curves of W32 and W32EB (W32EH) at the same current density and then divided by the oxide thickness, i.e., 4 nm. The barrier oxide field increases linearly with the applied electric field at low fields and then saturates at high applied fields. At low applied fields, part of the electrical charge is trapped close to the ML/barrier interface. In the case of W32HB this trapped charge is negative, while in the case of W32EB, the charge is positive. This is supported by our capacitance-voltage (*C-V*) experiments. The *C-V* characteristics show a hysteresis behavior (inset in Fig. 3). The hysteresis is clockwise for W32HB meaning the trapping of net negative charge at the ML/barrier interface. In contrast, the *C-V* hysteresis is counterclockwise for W32EB, meaning the trapping of net positive charge. The amount of the net trapped charge in W32EB is larger than in W32HB, which is supported by a difference in the *C-V* hysteresis width.[10] The tunneling mobility and the barrier height are larger for holes than for electrons. Therefore the net trapped positive charge is larger than the negative charge. The screening of the applied electric field by the trapped charge at the ML/barrier interface is larger and the voltage drop in the barrier oxide is smaller in W32EB than in W32HB.

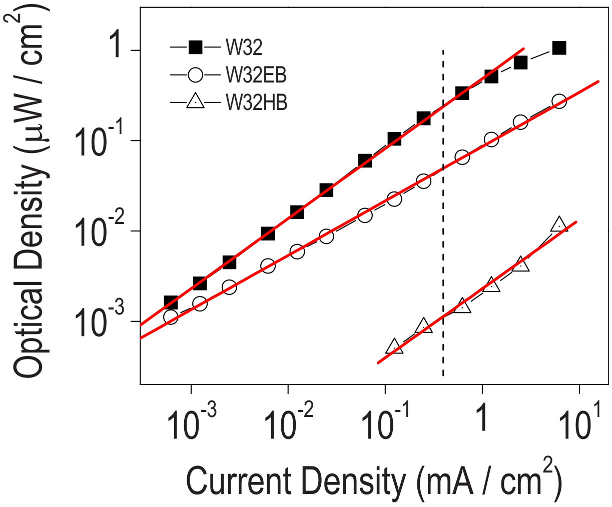

FIG. 4. (Color online) Optical power density as a function of current density for the MLs shown in the Fig. 3. The dashed line indicates the onset of FN tunneling.

When the electric field across the barrier oxide in W32HB reaches the value of around 7.5 MV/cm, the oxide electric field pins because the accumulated electrons at ML/barrier interface start to tunnel into the conduction band of silicon oxide via the FN mechanism. In contrast, the linear regime in W32EB extends to larger applied electric fields because larger fields are required for the FN tunneling of holes. At the applied electric field of about 3.5 MV/cm (7.5 MV/cm across the barrier oxide), the field-enhanced FN tunneling of electrons becomes the dominant injection mechanism in both W32EB and W32HB. Above this threshold, the same current densities in W32HB and W32EB are observed (Fig. 3).

The light-current characteristics of the three devices are shown in Fig. 4. Very weak light emission from W32HB device is observed under high applied electric fields only. Even under the FN tunneling regime, the light emission is about two orders of magnitude lower than that from W32. In the direct tunneling regime, the light emission from W32EB starts at an applied field of about 1.5 MV/cm (the current density is lower than 1 $\mu\mathrm{A/cm}^2$) and is much stronger than that of W32HB. This shows that indeed the holes are more difficult to inject than the electrons. In W32HB the oxide barrier blocks the injection of holes into the Si-nc and no electroluminescence (EL) emission is observed. When the applied electric field across the ML reaches the value of the field-enhanced FN tunneling, 3.5 MV/cm, weak EL signal appears which we attribute to impact ionization of electrons injected from the top electrode.

The slope of the light-current characteristic is related to the internal quantum efficiency (i.e., the ratio of the radiative emission rate to the sum of radiative and nonradiative emission rates). From Fig. 4, W32EB has a smaller slope than W32, 0.60 ± 0.01 versus 0.77 ± 0.01, respectively. This difference in the slope values might be attributed to the hot carrier injection that takes place in W32EB. The presence of the oxide barrier at the top of the Si-nc ML and the accumulated positive charge at the Si-nc ML/barrier interface create an extra electric field across the oxide layer that accelerates the injected electrons. W32HB shows the same slope as W32, namely 0.77 ± 0.05. There is no extra acceleration of the injected electrons from the gate and the radiative to nonradiative rate ratio in the W32HB is equal to the rate ratio in W32.

In conclusion, we demonstrated that bipolar charge injection in ML Si-nc LED yields the highest power efficiency. The electrons and holes are injected into Si-nc from both top and bottom electrodes through the direct tunneling mechanism. This study also shows that the limiting phenomenon is the injection of holes. Although the efficiency of our Si-nc LED is the highest, there is still room left to improve it and to reach a predicted value of 10% for similar device.[11]

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[10] The flatband voltage shift is proportional to the product of trapped charge and the centroid of charge distribution (or average charge distance from the gate-oxide interface). The average charge distance is different in the case of W32HB and W32EB. Let it be 25 nm (the nominal thicknesses) in the case of W32HB, and 4 nm in the case of W32EB. Then, if the amount of the trapped charge is the same, the flat-band voltage shift will be larger in W32HB that W32EB to the amount of 25/4. This is opposite to our results. Thus, the amount of the trapped charge must be different, and such that larger net charge is trapped in W32EB.
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