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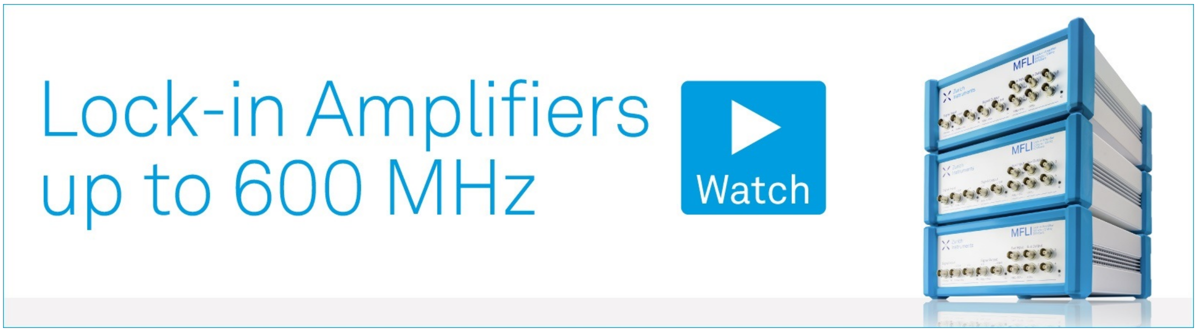

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Exciton-related electroluminescence from ZnO nanowire light-emitting diodes

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The authors study the microscopic origin of the electroluminescence from zinc oxide (ZnO) nanowire light-emitting diodes (LEDs) fabricated on a heavily doped *p*-type silicon (*p*-Si) substrate. By comparing the low-temperature photoluminescence and electroluminescence of a single nanowire LED, bound- and free-exciton related recombination processes, together with their longitudinal-optical phonon replicas, can be identified as the origin of both electroluminescence and photoluminescence. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3157274]

Semiconductor nanowires offer interesting possibilities in the area of photonics.[1–9] Nanowires are naturally anisotropic structures which, given certain dimensional constraints, can support waveguide modes and even lasing.[8] An even more intriguing prospect is that of combining widely different semiconductor materials, such as direct band-gap materials and silicon, without the need for wafer bonding technology.[10–12] In particular, we have recently demonstrated the fabrication of nanowire light-emitting diodes (LEDs) on a heavily-doped *p*-type silicon (*p*-Si) substrate, using nanowires of the wide-band-gap semiconductor zinc oxide (ZnO). ZnO is a material well suited for the development of ultraviolet (UV) optoelectronic devices[13] due to its large exciton binding energy.[14] Using high-temperature vapor-liquid-solid growth techniques, nontoxic and relatively inexpensive routes for the fabrication of high-quality ZnO nanowires have been demonstrated in recent years.[15] These ZnO nanowires have been shown to exhibit carrier densities of about $N=10^{17}$ cm^{-3} at room temperature and distinct bound exciton-related photoluminescence (PL) emission lines at liquid-helium temperatures.[16,17] Despite this, the evidence of excitonic recombination in electroluminescent ZnO devices has been indirect, and inferred from a peak emission energy smaller than what one would expect for band-to-band recombination.[12,18–21]

The main drawback of the ZnO material system is the lack of reproducible, stable, high-quality *p*-type doping with a reasonable concentration, which is required for most optoelectronic applications.[13] In our recent demonstration, the heterojunction is formed between the *n*-ZnO nanowire and a *p*-Si substrate.[12] If the *p*-Si native oxide is not removed before the fabrication of the nanowire devices, it acts as a tunnel barrier between the two semiconductors.[10,11] With an applied external bias, holes can tunnel from the valence band of the *p*-Si into the valence band of the ZnO nanowire. For such devices, UV electroluminescence (EL) has been observed at room temperature with the output intensity showing an almost linear dependence on the current flowing through the nanowire LED. In this paper, we study the microscopic processes that are involved in the radiative recombination of electrons and holes in *n*-ZnO/*p*-Si nanowire LEDs.

Details about the synthesis of the ZnO nanowires have been presented elsewhere.[15] In short, single crystalline ZnO nanowires were synthesized by a vapor-liquid-solid growth technique in a horizontal tube furnace at temperatures between 1000 and 1350 °C. The as-grown wires are typically 10–30 μm long and 100–350 nm in diameter. The nanowire LEDs were fabricated with a method similar to that described in Ref. 12 (the differences are described below). After growth, the nanowires were dispersed onto a heavily doped *p*-type silicon substrate ($\sim 10^{19}$ cm^{-3}) covered with a native layer of SiO_2. An 80 nm thick film of hydrogen silsesquioxane (HSQ, also known as spin-on glass, obtained as FOx-12 from Dow Corning) was then spun onto the substrate, resulting in a film profile in which the HSQ film is thinner on top of the nanowires than in the spaces between them. After cross-linking the HSQ with an electron beam writer (we use a dose of 300 μC/cm^2), the film was thinned down by $\sim$35 nm by reactive ion etching, which results in the top surfaces of the nanowires being exposed but not the silicon substrate. Finally, Ti(10 nm)/Au(100 nm) contacts were deposited with an electron beam evaporator. The schematics of the nanowire LEDs are shown in Fig. 1.

The samples were mounted inside a helium flow cryostat equipped with a temperature controller and an optical port. The external voltage was applied between the top metallic

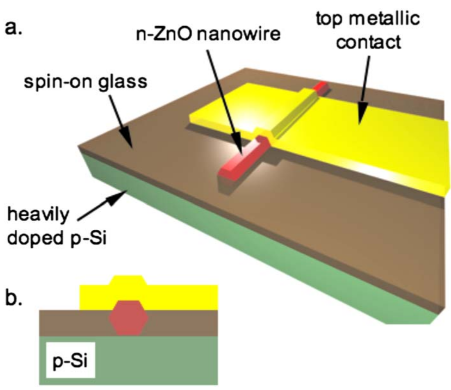

FIG. 1. (Color online) Schematics of the *n*-ZnO/*p*-Si nanowire LEDs. (a) Top view, (b) cross-sectional view.

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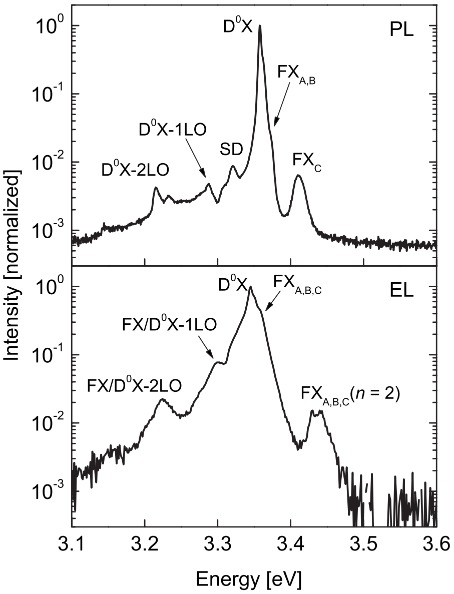

FIG. 2. PL and EL spectra of a ZnO nanowire LED recorded at 6 K. The PL was measured under excitation with a HeCd laser (325 nm), while for the EL a bias of 6 V (50 μA current) was applied. The main emission lines are assigned to the neutral donor-bound exciton (D^0X) and the FX as well as their LO phonon replicas (1 LO and 2 LO).

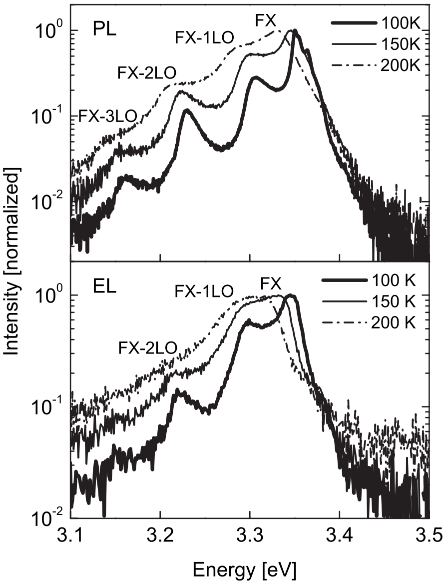

FIG. 3. PL and EL spectra of a ZnO nanowire LED recorded at temperatures between 100 and 200 K. The main emission lines are assigned to the FX and its LO phonon replica (1 LO, 2 LO, and 3 LO).

contact and the silicon substrate with a Keithey 2400 source/meter. The EL and PL were collected with a 36× reflective microscope objective with an aluminum coating (to optimize UV transmission) coupled to a 1/4 m spectrometer (150 lines mm^{-1} grating) and a thermoelectrically cooled charge coupled device camera (InstaSpec IV 78437 open electrode). For the PL measurements, the nanowires were excited with a HeCd laser (325 nm; cw) that was focused onto a single nanowire device through the same objective.

PL and EL spectra of a single-nanowire LED, being representative of the majority of fabricated devices, are shown in Fig. 2 on a logarithmic intensity scale for the near-band-edge region. The spectra reveal clear and distinct exciton-related emission lines where in both cases neutral donor-bound exciton (D^0X) recombination processes dominate the emission at 6 K. This is typically observed in the PL spectra for single crystalline ZnO nanowires that possess donor densities on the order of 10^{17} cm^{-3} as the nanowires used in this work.[16,17,22] At low temperatures, emission from free excitons (FX) is only visible as a shoulder on the high energy side of the dominating D^0X emission line because, with their low thermal energy, most excitons are trapped at the sites of the shallow donors. Other emission lines on the low energy side of the main D^0X band are known to be related to structural defects or to the longitudinal optical (LO) phonon replicas of the free and bound excitons.[22,23] Both the PL and EL spectra also show an additional emission band on the high-energy side of the FX emission. In the PL spectrum, this band is centered at around 3.42 eV. In the EL spectrum, however, it is centered at around 3.44 eV and also exhibits a multipeak structure. For excitonic emission in ZnO, two different processes can be responsible for these emission bands: the multipeak structure at around 3.44 eV in the EL spectrum suggests emission from excited exciton states ($n=2$), which can have contributions from the A, B and C excitons.[24] On the other hand, the emission at 3.42 eV in the PL spectrum can be attributed to the radiative recombination of the C exciton in its ground state.[24] The C exciton emission is only allowed for electric fields parallel to the *c*-axis of ZnO[13] and therefore can be expected to contribute to the PL spectrum of our dispersed nanowires more strongly than to the EL spectrum.

In general, the PL and EL spectra present similar structure, with the EL spectrum shifted to lower energies by about 12 meV and also exhibiting slightly broader emission lines, as determined by the full width at half maximum (FWHM). In particular, the main D^0X band has a FWHM of 4 meV in the PL spectrum and 7 meV in the EL spectrum. This difference may be accounted for by a higher local temperature for the EL due to electrical heating, which can be supported by two separate arguments. The 12 meV redshift in the EL spectrum corresponds to a temperature increase of about 50 ± 30 K (Ref. 25), assuming a purely thermal effect. In addition, the relative intensities of the FX shoulder and the main D^0X band are different: in the PL spectrum, we find a ratio of $I_{FX}/I_{D^0X}=0.03$, while in the EL spectrum, the ratio is $I_{FX}/I_{D^0X}=0.39$, i.e., in EL a significantly higher fraction of excitons is thermally activated from the donor localization centers. More specifically, by measuring the PL spectrum of a nanowire and calculating the ratio I_{FX}/I_{D^0X} as a function of temperature, we find that $I_{FX}/I_{D^0X}=0.39$ corresponds to a temperature of approximately 60 K. Thus, we conclude that the local temperature in our LED, placed on a substrate at 10 K, can be increased by approximately 50 K under a 6V, 50 μA (300 μW) bias.

The PL and EL spectra of the single nanowire LED at higher temperatures reveal a continuous increase of the intensities of the FX lines together with their LO phonon replica, as can be seen from the results shown in Fig. 3. The general redshift of the spectra with increasing temperature can be ascribed to the temperature dependence of the ZnO band-gap.[25] In addition, the PL emission at temperatures above 150 K is clearly dominated by the FX emission. At 200 K and above, the FX band merges with its LO phonon replica, resulting in an asymmetric shape of the PL emission.

In contrast, in the EL spectra at $T > 150$ K the FX band shows a comparable intensity with its 1 LO side band which is distinctly more pronounced than in the PL spectra. This results in a slight redshift of the overall EL emission band at 200 K when compared to the PL emission taken at the nominally same temperature. The difference between the PL and EL spectra is most likely due to the current flowing through the nanowire LED, which we expect to cause greater heating compared to the PL measurements, as already observed for $T = 6$ K. Still, our results clearly demonstrate that the EL from n-ZnO/p-Si nanowire LED stems from excitonic recombination processes.

In summary, at $T = 6$ K, D^0X emission dominates the EL, whereas at temperatures above 150 K, the FX, together with its LO phonon replica, are responsible for light emission.[17] In conclusion, we have studied the microscopic origin of EL from ZnO nanowire LEDs. We have found clear evidence for exciton-related emission processes that dominate the near band-edge emission of the nanowire LED at temperatures between 6 and 200 K. At low temperatures, donor bound exciton-related emission lines are observed both in PL and EL. We conclude that the nanowire is heated by about 50 K during the electrical operation with 300 μW of electrical power. Still, due to the relatively large binding energies of the exciton complexes in ZnO, efficient excitonic recombination processes persist. At higher temperatures, the FX emission together, with its first LO phonon replica, dominated the EL emission spectrum. Our results demonstrate that n-ZnO/p-Si nanowire LED operate with efficient excitonic recombination processes and should provide high internal quantum efficiencies leaving the tunnel injection of holes into the nanowires as the main limiting factor.

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