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Flexible Inorganic Nanowire Light-Emitting Diode

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ABSTRACT

We report a highly flexible light-emitting device in which inorganic nanowires are the optically active components. The single-crystalline ZnO nanowires are grown at 80 °C on flexible polymer-based indium-tin-oxide-coated substrates and subsequently encapsulated in a minimal-thickness, void-filling polystyrene film. A reflective top contact serving as the anode in the diode structure is provided by a strongly doped p-type polymer and an evaporated Au film. The emission through the polymer side of this arrangement covers most of the visual region. Electrical and optical properties as well as performance limitations of the device structure are discussed.

Nanoscale hybrid materials containing organic as well as inorganic components have attracted considerable research interest in recent years, as they promise new properties that may not easily be available from conventional materials. For example, combining the high flexibility of polymers with the structural and chemical stability of inorganic nanostructures may lead to new flexible, possibly elastic devices with the high functional stability of inorganic components.[1,2] The simple processing and the possibility of tailoring optical and electrical properties in both types of materials have raised hopes to obtain cost-efficient large area devices. Most recently, the extended interface areas available in nanohybrid thin films have been found to exhibit highly efficient charge-transfer processes[3] and strong optical effects[4,5] that are not observed in homogeneous materials or more simply structured arrangements. These new discoveries are now being explored for photovoltaic devices, sensors as well as light-emitting diodes, waveguides, nonlinear optical devices, filters, and other devices.

In this paper, we report a novel light-emitting diode (LED) structure that uses vertically oriented ZnO nanowires grown on a flexible transparent substrate and embedded in a polymeric matrix. Single-crystalline inorganic nanowires are the optically active component in this device structure, while the polymeric environment provides a robust, yet flexible support matrix. This flexible hybrid LED generates a broad emission spectrum covering most of the visible range and reaching to the near-ultraviolet. The optically active components in this flexible and potentially stretchable device are inorganic nanowires, making this structure an interesting alternative to all-organic electronic and photonic devices.

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Figure 1 shows the design scheme of the flexible LED structure. A transparent polyethylene terephtalate (PET) foil covered with a sputtered indium-tin-oxide (ITO) layer of 10Ω sheet resistance is used as a supporting substrate. Vertically oriented single-crystalline ZnO nanowires are monolithically grown in electrodeposition on the ITO layer using a standard three-electrode electrochemical setup with a saturated Ag/AgCl reference electrode and a Pt foil as a counter electrode.[6] The electrodeposition is carried out at 80 °C in an aqueous electrolyte containing 3 mM $ZnCl_2$, 5 μM $AlCl_3$, and 0.1 M KCl. Oxygen bubbling and magnetic stirring are provided during the electrodeposition to produce an oxygen-saturated electrolyte solution. Typical deposition potentials are −0.95 V. Addition of $AlCl_3$ to the electrolyte has been found to improve the conductivity of the nanowires[7] and to lead to increased emission intensities.[8,9] After ∼1 h of deposition, a homogeneous coverage of vertically oriented ZnO nanowires is obtained. The nanowires are typically ∼2 μm in length and 70−120 nm in diameter, as shown in Figure 2.

After deposition the nanowire films are rinsed in pure H_2O, dried in N_2, and then embedded in an insulating polystyrene (PS) film that is spin-coated from a polystyrene/toluene solution.[8] The spin-coating parameters are optimized as to completely fill out the space between the nanowires and produce only a very thin coverage of the nanowire tips, as shown in Figure 3. Typical tip coverages are less than 20 nm. Radio frequency plasma etching in N_2 or O_2 can be used to further reduce the polystyrene layer thickness at the tips. A top contact consisting of a thin poly(3,4-ethylene-dioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer and an evaporated Au film are provided to serve as the hole injection anode in the LED.

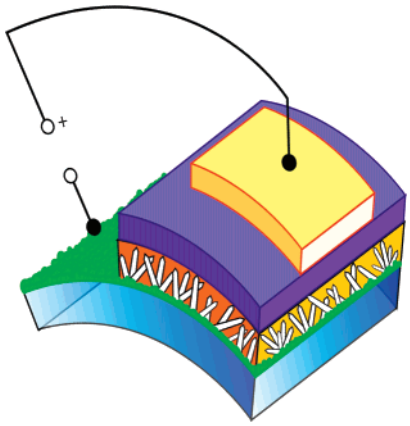

Figure 1. Design scheme for a flexible LED structure consisting of vertically oriented single crystalline nanowires grown on a polymeric ITO-coated substrate. The top contact consists of p-type polymer and an evaporated Au layer. Light is emitted through the transparent polymer.

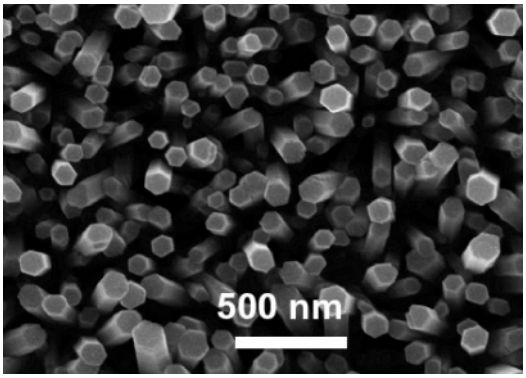

Figure 2. ZnO nanowires grown in electrodeposition on a planar transparent substrate.

Electrodeposition of ZnO nanowires has previously been carried out on doped SnO_2, $InSn_2O_3$, Au, Cu, and on n- and p-doped Si substrates.[10] In all cases, the wires are usually found to be robustly attached to the substrate. They remain attached even as the substrate is bent over very small curvature radii. Figure 4 shows ZnO nanowires adhering to a thin Au film that separated from a glass substrate in the drying process following the nanowire deposition. In this case the curvature radius of the film is less than 10 μm.

Figure 5a,b shows electroluminescence spectra for undoped and Al-doped nanowires on a flexible ITO-coated substrate in comparison to spectra obtained on planar SnO_2-coated glass substrates. The spectra from the flexible devices have slightly less intensity, but the spectral distribution is qualitatively similar to those on solid substrates. The undoped ZnO nanowires on the flexible foils show a broad emission band covering the range 500−1100 nm with a peak that is slightly red-shifted from the spectra obtained on the glass substrates. Al-doping in the range of 5 μM reduces the red-shift. We previously found that annealing of Al-doped nanowires at ∼300 °C increases the emission intensity and produces ultraviolet emission line at 390 nm. On the PET foils used here, annealing could only be carried out up to 150 °C, and the ultraviolet emission was therefore not observed. We expect ultraviolet emission to occur, however, when more robust polymer substrates are used, such as kapton, which is stable to approximately 500 °C.

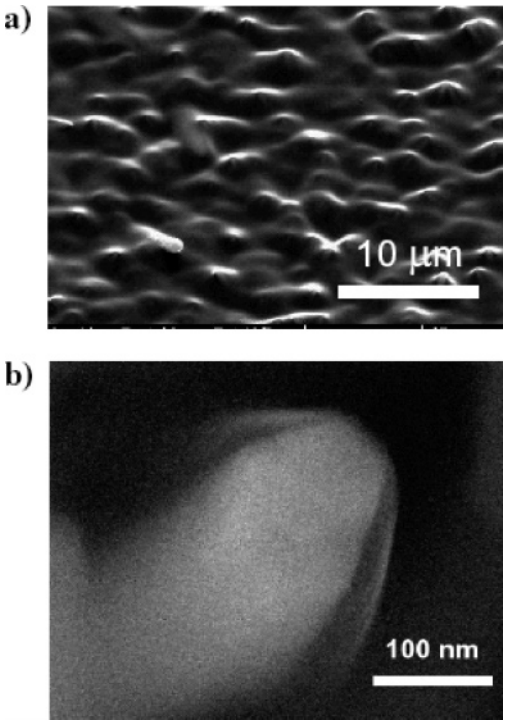

Figure 3. Nanowires spin-coated with polystyrene from a polystyrene/toluene solution. (a) Overview and (b) coverage at a single nanowire tip with a thickness of ∼15 nm.

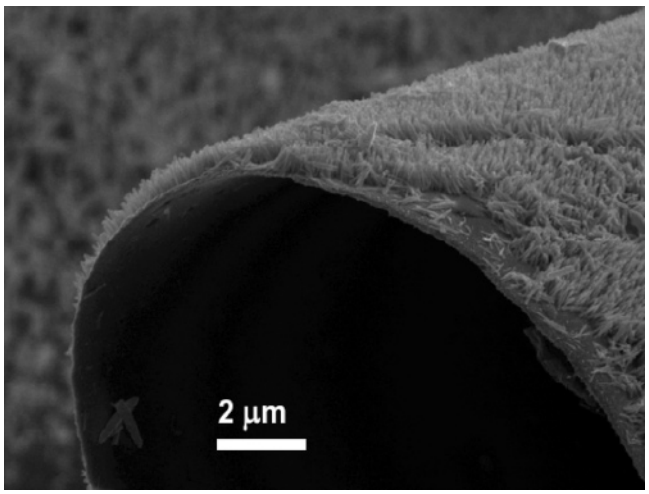

Figure 4. Nanowires on a bent Au film with curvature radius of <10 μm.

Figure 5c,d shows the current−voltage for the flexible LEDs. The diode characteristics and the rectification is mainly produced at the back contact, which is a n^--i-p^+ heterojunction with the layer sequence, ZnO/PS/PEDOT:PSS/Au. As this contact is identical for the flexible and the planar LEDs, it is surprising to find the forward currents in the flexible devices to be higher than those obtained on planar SnO_2/glass substrates. However, the n^--i-p^+ junction limits the forward currents only for voltages below approximately 1 V forward. For larger voltages, that is, in all of the operating regime of the LED, the currents are proportional

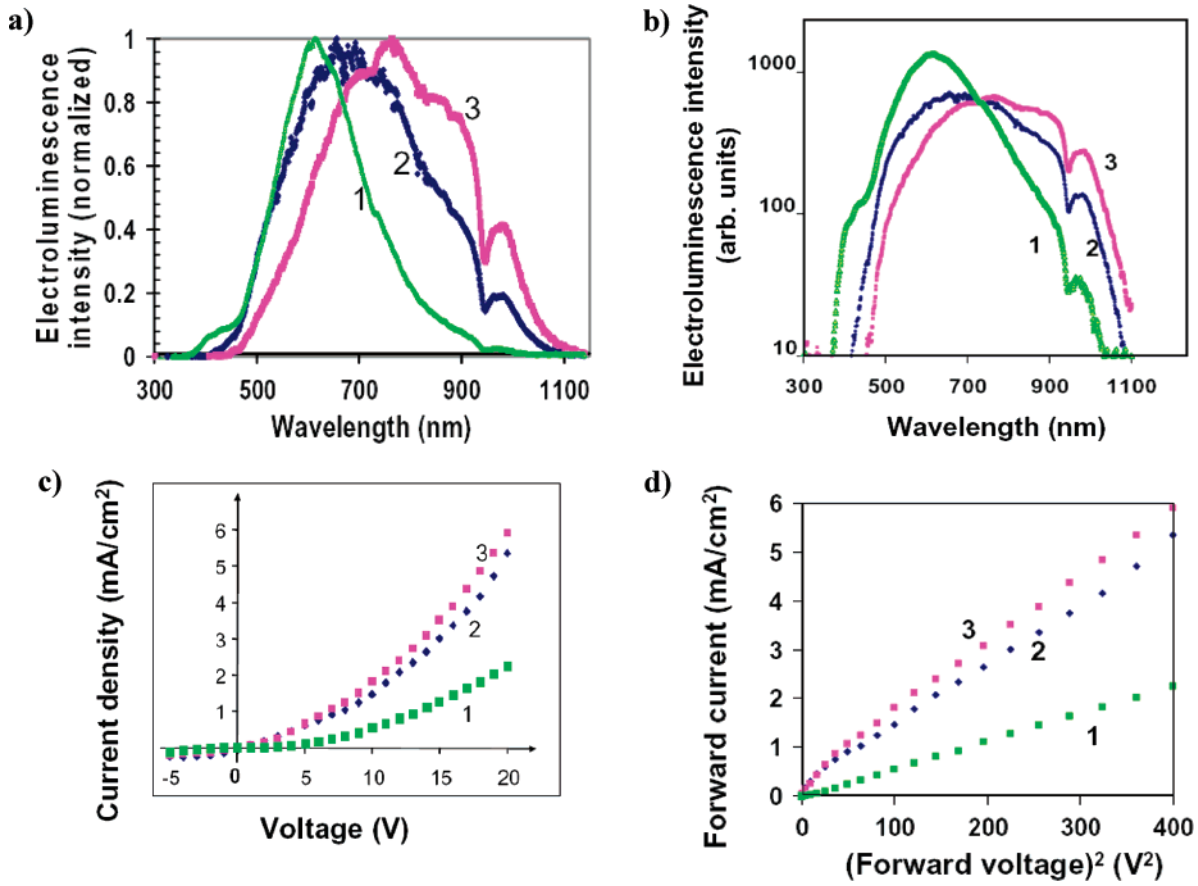

Figure 5. Optical and electrical performance of the flexible LED. (a) Normalized electroluminescence spectra for various LED structures; (b) logarithmic plot of the emission spectra from various LED structures; (c) electrical characteristics of various LED structures; and (d) current vs (voltage)^2 indicating space-charge-limited current characteristics for $V_{forward} > 3$ V. Curves 1: undoped nanowires grown on SnO_2-coated glass substrates. Curves 2: Al-doped nanowires grown on flexible ITO-coated PET foils. Curves 3: Undoped nanowires grown on flexible ITO-coated PET foils.

to the voltage squared, as shown in Figure 5b. The natural explanation for this dependence is in terms of space-charge limited injection into the ZnO, as expressed by the Mott−Gurney law,[11] $i(V) = 9/8\ \epsilon\mu\ (V^2/L^3)$, with ϵ being the permittivity, μ is the carrier mobility, and L is the nanowire length. The high accuracy of the square law in the experimental data suggests that the nanowires are essentially trap-free.

The differences in current density observed for the flexible LEDs and those on glass substrates suggest that the current is not strongly influenced by traps. Electron microscopy indeed confirms that the nanowires in the flexible structure are approximately 35% shorter than those on the planar devices. This is likely due to different growth conditions on the two types of substrates. To confirm the validity of the Mott−Gurney law, we have intentionally altered the nanowire length by varying the deposition time. Figure 6 shows that the expected L^{-3} dependence holds as expected. This finding indicates that the forward current in these diodes is neither barrier- nor diffusion-limited but depends on the nanowire length. The Mott−Gurney law also allows a determination of the carrier drift mobility. Estimating the nanowire coverage to be of the order of 50% gives $\mu = 2 \times 10^{-3}$ cm^2/Vs.

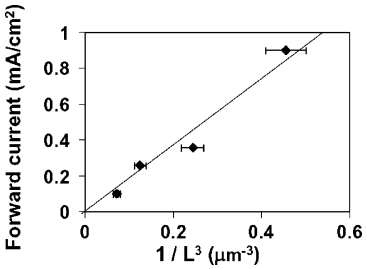

Figure 6. Dependence of the forward current at $V_{forward} = 10$ V on nanowire length L. The forward current is approximately proportional to $1/L^3$ as expected from the Mott−Gurney law.

The comparison of the emission characteristics shows that the different substrates have only a minor effect on the optical performance of the wires. In all structures, flexible and conventional, the electroluminescence typically sets in at a forward bias of ~3 V, and this threshold value is likely set by the dielectric breakdown in the thin residual polystyrene at the nanowire tips, which is expected to occur at a field strength of $\sim 10^7$ V/cm. To obtain larger brightness, a monolithic inorganic p-n homo- or heterojunction contact would clearly be most desirable. Several research groups are developing such junctions, and first implementations have been explored in continuous thin film devices. Yet a

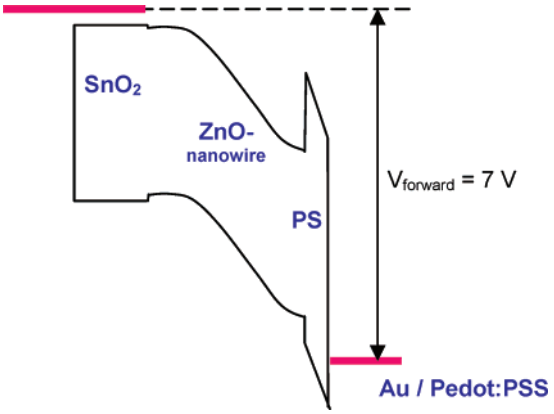

Figure 7. Schematic energy diagram of the LED under operating conditions at ~7V forward bias.

monolithic nanowire device involving a low-resistance p-n junction to ZnO has not been achieved.

In Figure 7 we show a schematic energy diagram of the LED under operating conditions. This diagram is based on band gap and electron affinity values obtained from refs 12−14. The diagram shows a degenerately doped ITO layer with a conduction band edge close to that of the ZnO nanowires. While there is considerable bandbending at the ITO/ZnO interface at zero-applied voltage due to the large differences in doping concentrations, the diagram indicates unobstructed electron injection at forward voltages of ~7 V. The back contact of the LED is shown to incorporate a high-energy tunneling path for hole injection through the large polystyrene band gap. Such a tunneling path would explain the possibility of ultraviolet electroluminescence. It is also consistent with our conclusion that the hole-injection contact would need modification in future devices.

To conclude, a simple route toward a flexible light-emitting device based on inorganic nanowires as the active optical component has been explored. The new device exibits electroluminescence over most of the visible spectrum at moderate forward bias. In operation, space-charge-limited electron transport through the nanowires is observed. The electrical characteristics indicate that the threshold voltages for the onset of the luminescence are determined by breakdown in the n-i-p back contact. A monolithic n-p junction and higher nanowire bulk doping appear as the next development goals for improved efficiency in these devices.

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