Zinc oxide nanorod-based heterostructures on solid and soft substrates for white-light-emitting diode applications

M Willander¹, O Nur, N Bano and K Sultana
Department of Science and Technology (ITN), Campus Norrköping, Linköping University, SE-601 74 Norrköping, Sweden
E-mail: magwi@itn.liu.se

New Journal of Physics 11 (2009) 125020 (16pp)
Received 13 June 2009
Published 17 December 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/12/125020

Abstract. ZnO nanorods with excellent optical and electro-optical emission characteristics were grown using high- and low-temperature techniques on solid and soft substrate materials. The solid crystalline substrates included p-4H-SiC and p-GaN, while the soft amorphous substrates included p-type polymers deposited on glass and flexible plastic. Two different growth approaches were used to produce these samples. We used the vapor–liquid–solid (VLS) technique (high temperature) and aqueous chemical growth (ACG), which is a low-temperature technique. These ZnO nanorod samples were characterized by room temperature photoluminescence (PL) and processed to fabricate light-emitting diodes (LEDs). The LED characteristics were further investigated by I–V and electroluminescence (EL). As observed by PL measurements, all samples revealed a sharp narrow ultraviolet (UV) peak due to band-edge emission, indicating the good crystalline quality of the grown ZnO nanorods. The origin of the different peaks within the visible region was correlated to different deep level defects reported earlier for ZnO. All fabricated LEDs showed EL providing a wide band extended through the whole visible spectrum and hence produced clear white light observable to the naked eye. The emitted color quality investigation showed that superior color quality was manifested in a high color rendering index and stable color under current variation, indicating that these heterojunction and hybrid LEDs have potential for the development of future light sources. The ZnO nanorod-based LEDs grown by low-temperature ACG on glass and flexible plastic can, after further development, be candidates for future large-area white-light sources.

¹ Author to whom any correspondence should be addressed.
1. Introduction

Hexagonal zinc oxide (ZnO), being a direct wide bandgap material with a bandgap of 3.4 eV and a relatively large exciton binding energy of 60 meV, both at room temperature (RT), has attracted renewed global interest due to the fact that it also possesses a rich family of nanostructures that can be obtained on a variety of substrates using different growth methods [1]. In addition, ZnO is piezoelectric [2] and is biocompatible and bio-safe [3]. The growth of ZnO in its nanostructure form can be achieved using different high- as well as low-temperature (<100 °C) methods [4]. Among the most common high-temperature techniques used is the vapor–liquid–solid (VLS) approach, which was developed more than 40 years ago [5]. We employed this technique and achieved a variety of different ZnO nanostructures [6]. The low-temperature techniques are restricted to the aqueous chemical growth (ACG) method [7, 8].

An important property of the ZnO semiconductor is that it possesses a large number of radiative intrinsic and extrinsic deep level defects [9]. Specifically, ZnO, in addition to the ultraviolet (UV) emission due to the bandgap, emits blue, green, yellow and orange-red colors [10, 11], i.e. it covers the whole visible region. This is why the RT photoluminescence (PL) spectrum of ZnO is characterized by a sharp UV peak at around 380 nm, and a wide broad band extending laterally between 400 nm and up to 700 nm. The dominant emitted color depends on the growth method and its parameters and this implies that the emitted color line can be controlled [10]. Hence ZnO is of great potential for development of white-light-emitting sources. The main problem for the application of ZnO in opto-electronic devices is the ambipolar doping, a problem found frequently in wide-bandgap materials [9]. This problem implies that while one type of doping is easy, the other is difficult to obtain. In the case of ZnO, it is the n-type doping which is easily achieved, while the p-type doping is difficult. Elements from group I are, according to theory, acceptors on the Zn sites, and group V can be acceptors on the O sites and should in principle provide p-type conductivity. Nevertheless, to date no low-resistivity, stable and reproducible scenario has been demonstrated, mainly due to the compensation of acceptors by shallow donors [12, 13].

As ZnO has a tendency to self-organized growth, it turns out that it is quite easy to grow high-quality ZnO nanostructures on a variety of substrates, regardless of the lattice mismatch between the ZnO and the substrate. The small footprint and the relatively large surface-area-to-volume ratio, together with the self-organized growth property, have all led to the fact that the growth of ZnO nanorods is achievable on almost any substrate, even those of an amorphous nature. In this connection, we focus the light-emitting diodes (LEDs) development...
by using external p-type substrates. There are different options for the external p-type side of the junction to be combined with n-ZnO nanorods to form heterojunction LEDs. Among the possible candidates, we are focusing on p-4H-SiC, p-GaN, and on organic p-type polymers to form organic–inorganic hybrid junctions. The advantage of using p-4H-SiC and p-GaN is in the similarity of the lattice structure of the two materials to that of ZnO (all three materials have hexagonal structure). This will in turn lead to easier growth and will allow the alignment of the ZnO to be achieved. In addition to this, the use of p-GaN will also allow the utilization of the strong blue emission of GaN combined with the ZnO deep-level emission (DLE) (see discussion on the color quality in section 3.3 below). Moreover, the choice of the p-type polymers deposited on glass and plastic will have many advantages. Among them is the possibility of growing the ZnO using the low-temperature approach (see below) on large substrates and hence with the potential for developing large-area white-light emitting sources. In addition, and owing to the fact that in organic LEDs the n-type electrode is usually not stable, the use of n-ZnO as electron injector will stabilize the n-electrode, and the advantages of utilizing emission from both sides of the hybrid junction can then be gained. Considering the emission, we are interested in the DLE from ZnO as it can provide a spectrum that covers the whole visible region and hence produce white light as will be shown below. Many authors have demonstrated n-ZnO/p-type substrate EL using different p-type substrates. A recent example is the use of ZnO nanorods grown on a polymer- and indium tin oxide- (ITO) coated substrate [14].

In this paper, we will show recent results from the growth of ZnO nanorods on four different substrates. These are p-SiC, p-GaN, PEDOT:PSS/p-type polymer(s) on glass and on flexible plastic. Moreover, results for LEDs fabricated from these heterostructures will be shown and discussed. The advantages gained, e.g. the use of PEDOT:PSS as a replacement for the commonly used ITO as a contact layer, will all be discussed. The results include electrical characteristics, optical characteristics and electro-optical results.

2. Growth of ZnO nanorods

We will here briefly describe the two growth techniques used to obtain ZnO nanorods on the different crystalline as well as amorphous substrates presented here. These are the VLS as an example of high-temperature approach and the ACG as a low-temperature approach. Figure 1 shows the schematic diagram of the final processed LEDs. In VLS growth a substrate covered with a thin (2–8 nm) layer of catalytic metal (gold in this case) is inserted into an oven and placed beside a boat that contains high purity (99.9%) ZnO powder mixed with graphite (99.9%) at a ratio of 1 : 1. The temperature of the growth is usually around 850 °C, although growth using
the VLS approach has been achieved at temperatures below and above this value. Usually the substrate covered with the thin metallic catalyst layer is placed at a small distance (around 10 cm) from the boat with the source material at the carrier gas (Ar) downstream side. Gold will cluster and initiate growth nucleation. The growth temperature as well as the Au layer thickness will affect the morphology and dimensions of the grown ZnO nanorods. Moreover, oxygen partial pressure in the oven was also demonstrated to play an important role in the alignment of the grown ZnO nanorods.

The other promising technique to be presented is the low-temperature ACG method forming p–n heterojunctions. There are many different chemical growth methods for ZnO nanostructures. The most common method is described by Vayssieres et al [15], in which zinc nitrate is mixed with hexa-methylene-tetramine (HMT). An equimolar concentration of HMT and zinc nitrate 0.022–0.075 mM is used. The substrate is placed in the solution and heated to 90–96°C for 2–4 h. To improve the quality of the grown ZnO NRs, this method was combined with the substrate preparation technique developed by Greene et al [16]. The method developed by Greene et al is based on the deposition of textured ZnO nano-particles of a thickness of around 10 nm before growth. The purpose of this method is to improve the verticality of the grown ZnO nanorods on arbitrary substrates. Spin coater was used to deposit a thin and uniform seed layer. The seed layer coating process was repeated three times to get a uniform layer. Then the substrate was heated in air at 250°C for 20 min.

Figure 2 shows typical scanning electron microscope (SEM) images of ZnO nanorods grown on different substrates by the above mentioned two methods. Figure 2(a) shows ZnO nanorods grown on p-4H-SiC thin layer with acceptor concentration around 5 × 10¹⁸ cm⁻³ grown by chemical vapor deposition on n-SiC commercial substrate. For the ZnO nanorods shown in figure 2(a) we adopted the VLS technique. The ZnO nanorods were grown vertically aligned and with a length of 1.9–2.2 µm and a width of 400–600 nm. The inset in the figure displays an SEM image of the same sample during the LED fabrication just before deposition of the metal contact to the nanorods. As can be seen in the inset, an insulating layer is deposited to isolate the nanorods’ contact from the p-type SiC layer. In figure 2(b) the SEM image shows dense hexagonal ZnO nanorods grown by the ACG method described above on p-GaN substrates. As is seen in the figure, ZnO nanorods with diameters of 125–174 nm were achieved. Figures 2(c) and (d) show the morphology of ZnO nanorods grown by the ACG method on polymer multi-layers deposited on glass and plastic, respectively. As shown in figures 2(c) and (d) dense and notably vertical ZnO nanorods have been obtained.

3. Light-emitting diodes (LEDs) structure and characteristics

As mentioned above, we achieved device-quality ZnO nanorods on different substrates. Table 1 describes the different LEDs fabricated. All these LEDs showed emission spectra covering a large portion of the visible range and hence white-light emission was observed. Then PL measurements were performed to investigate optical emission and assess the quality of our grown ZnO nanorods. Here we show RT PL obtained by using laser lines with wavelengths of 270 or 350 nm from an Ar⁺ laser as the excitation sources. After growth, an SEM inspection was performed, followed by PL investigation, and the different samples were then processed to LEDs based on ZnO/p-type external substrates. In some cases before the growth (ACG samples) ohmic contact to the substrate was deposited and annealed. An insulator was deposited to avoid shortage between the top ZnO nanorods’ contact and the p-type substrate. For this we used
Figure 2. (a) A typical SEM image of ZnO nanorods grown by the VLS method on p-4H-SiC; the inset shows the same ZnO nanorods sample after the deposition of an insulator followed by oxygen RIE for the exposure of the nanorod tips for depositing metal contacts. (b) A top view SEM image showing hexagonal ZnO nanorods grown on p-GaN using the ACG approach. (c) ZnO nanorods grown on multi-layered p-type polymers spin-coated on glass; the structure sequence is poly(3, 4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/PVK/TFB/ZnO nanorods. (d) ZnO nanorods grown on polymer mulit layer(s) deposited on flexible plastic.

polystyrene and in some cases normal photoresist. After the deposition of the insulator reactive ion etching (RIE) was performed to expose the tip of the ZnO nanorods. Contacts were then deposited on to the ZnO nanorods. Alloyed as well as non-alloyed contact scenarios were used depending on the substrate. Finally, electrical characterization, followed by EL measurement, was performed for all LEDs to study the radiative recombination of carriers and complement the PL spectra. This is the first category of n-ZnO nanorods on solid substrates (on p-4H-SiC and p-GaN substrates); see table 1. The LED fabricated on p-SiC is denoted as LED1, while the one fabricated on p-GaN is denoted as LED2. The second category to be presented here is the hybrid n-ZnO/p-polymer LED, i.e. n-ZnO nanorods on soft material. These LEDs were fabricated using two-layer p-type-polymers deposited on glass (denoted as LED3) or flexible plastic (denoted as LED4) with top n-ZnO nanorods grown using the ACG method.

New Journal of Physics 11 (2009) 125020 (http://www.njp.org/)
Table 1. Description of the growth method and type of substrate used for the four different LEDs presented.

| LED # | Growth method | Substrate                  |
|-------|---------------|-----------------------------|
| LED1  | VLS           | p-4H-SiC (solid material)   |
| LED2  | ACG           | p-GaN (solid material)      |
| LED3  | ACG           | p-polymer/glass (soft material) |
| LED4  | ACG           | p-polymer/plastic (soft material) |

For all device configurations we used poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), which is denoted by PEDOT:PSS, as a bottom contact layer. The two polymer layers were a hole-transport layer and polymer-emitting layer. For the hole-transport and polymer-emitting layer we focused mainly on four different polymers; two famous blue-emitting materials were blended with other two polymers. Poly(9, 9-diocetylfluorene) (PFO), which is considered a promising blue emitting-material (band gap of 3.3 eV and highest occupied molecular orbital (HOMO) of 5.8 eV) [17], was added in a multilayer configuration with (4, 4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl) (NPD) (band gap of about 3.1 eV and HOMO of 5.5 eV) [18]. The NPD enhances the hole transport and also divides the hole energy barrier between the PEDOT:PSS and the PFO into two separate barriers, leading to an increase of the positive charge carriers (holes), and this increases the exciton recombination probability [19]. The second configuration was achieved using poly(N-vinylcarbazole) (PVK), which has a band gap of about 3.5 eV and the HOMO is equal to 5.8 eV [20], blended with poly(9, 9-diocetyl-fluorene-co-N(4-butylphenyl)diphenylamine) (TFB), which has a band gap of about 3.3 eV and the HOMO is equal to 5.3 eV. The TFB will increase the viscosity of the blended solution, and hence it improves the film quality. When using the blended solution we achieve three advantages: enhanced hole transport in the device; a wider emission range; it acts as an electron blocker with an offset of 1.2 eV [21]. On top of the polymer(s) structure, ZnO nanorods were grown by the ACG method as described above. This was followed by the deposition of an insulating layer, and finally a non-alloyed contact was evaporated on top of the ZnO nanorods using a shadow mask with circular dots.

3.1. Optical characteristics

The RT PL spectrum of ZnO nanorods grown on p-4H-SiC is shown in figure 3(a). A double grating monochromator and a photomultiplier detector were used to disperse and detect the ZnO nanowires emission. A laser line with a wavelength 350 nm from a cw Ar$^+$ source was used as the excitation source. As seen in figure 3(a), this PL consists of an intense narrow UV centered at around 380 nm and a defect-related wide band (420–700 nm). The appearance of the sharp narrow UV is an indication of the good quality of the ZnO nanorods; i.e. a well defined material with a bandgap of ZnO is achieved. It is extensively reported that this broad DLE band is a defect-related emission and that it is a superposition of different defect bands emitting in different wavelengths [22]–[24]. This is probably one reason for debate, since different samples have different defect configurations due to different growth methods and growth conditions. The peak position of the deep band emission is defined according to the relative density of these radiative defects. The radiative defects observed here lie within the deep band emission.
Figure 3. (a) RT PL spectrum for ZnO/p-4H-SiC (LED1) measured using an Argon laser operating at 150 mW at RT, (b) RT PL spectrum of ZnO nanorods grown on p-GaN commercial substrates (LED2) using the ACG method showing three different emissions.

(420–700 nm). Many different models have been proposed to explain the nature of the DLE. Klason et al \cite{23,24} showed the influence of zinc vacancy ($V_{Zn}$) and oxygen vacancy ($V_{o}$) related defects on the PL properties of an ‘undoped’ bulk ZnO. ZnO can exhibit different emissions in the visible range including violet, blue, green, yellow, and orange-red which are associated with intrinsic and extrinsic defects in the material. The above measured PL characteristics were also confirmed by cathodoluminescence (CL) measurements. CL measurements (not shown) performed on the same n-ZnO nanorods/p-4H-SiC structures revealed that both the UV and the DLE emissions were observed.

Figure 3(b) shows the PL spectrum for ZnO nanorods grown on p-GaN measured at RT. A laser line of wavelength 266 nm from a diode laser (Coherent Verdi) pumped resonant frequency doubling unit (MBD 266) was used as an excitation source. A dominant PL peak was observed at $\sim 378$ nm, which was attributed to the recombination of free exciton, i.e. band edge emission of ZnO nanorods \cite{25}. It can be clearly observed that the ZnO nanorods exhibit a broad defect-band emission centered in the red spectral region with the center at 700 nm (1.77 eV). The red emission peak can be attributed to interstitial oxygen defects \cite{26}. The related energy levels are thought to be deep donor and acceptor centers with strong electron–phonon interaction. The transition from the donor to the acceptor center is thus assumed to be responsible for the emission centered at red \cite{27}. But in our case a dominant PL peak was observed at $\sim 380$ nm, a shoulder at 550 nm, and a broad defect-band emission centered at 700 nm (1.77 eV) in the red spectral range extended to yellow, orange and green bands. The green emission 550 nm was also observed which may be due to the recombination of electrons at the conduction band with holes trapped in oxygen-related defects \cite{28}. The above PL characteristics were also confirmed using CL measurements (not shown here) revealing that emissions from both the GaN as well as the ZnO nanorods were observed.

The PL characteristics of the ZnO/p-polymer hybrid structures were measured at RT before and after the growth of the ZnO nanorods. The first PL measurements were performed as a reference measurement to distinguish the peaks’ origins in the fabricated LEDs.
Figure 4. RT PL spectrum of (a) NPD/PFO multi-layer polymer (b) PVK/TFB blend polymer, (c) NPD/PFO-ZnO nanorods (LED3) and (d) PVK/TFB/ZnO nanorods (LED4). The PL measurements were performed using Nd:YA6 laser with a wavelength of 280 nm.

Figures 4(a)–(d) show the PL spectra of the two different ZnO/polymer hybrid structures before (figures 4(a) and (b)) and after (figures 4(c) and (d)) the growth of the ZnO nanorods. The PFO main known peak with a maximum intensity at 458 nm is observed as expected [20]. This peak originates from excitonic emission and its vibronic progression from non-interacting single chains. In addition to this main peak, a low-intensity peak centered at around 700 nm is observed. This peak originates from the glass substrate as confirmed by the PL spectrum obtained from bare glass. Although the same glass was also used in the other configuration, the intensity of this peak was much lower even for the TFB-PVK polymer blended configuration. The reason for this is that the blended structure has a higher density, and spin coating resulted in a much thicker film than for the PFO-NPD multi-layer structure. For the PVK-TFB polymer blend the blue emission which corresponds to the PVK polymer material with a peak having a maximum intensity centered at 455 nm was observed [19]. The results after the growth of the ZnO nanorods show that the PL for the NPD-PFO/ZnO reveals both the polymer and the ZnO DLE. When the ZnO is grown on top of the NPD/PFO polymers, an extra peak centered at 554 nm is observed (figure 4(c)). This emission corresponds to the ZnO green emission band. Moreover, no shift in the PFO peak position was observed after the growth of ZnO nanorods,
but the intensity of the peak was only 30% of the intensity measured for the film before the ZnO nanorods’ growth. The PL spectrum of the TFP-PVK/ZnO nanorods configuration after ZnO nanorod growth (figure 4(d)) shows similar characteristics. Here again an extra peak centered at 568 nm is observed when ZnO is grown on top of the TFP/PVK blend. Although this peak is not exactly centered at 554 nm as for the first configuration, it also results from the presence of ZnO and originates from intrinsic defects. Both peaks (at 554 nm and 568 nm) lie within the broad green emission band. It is known that the peak position can be different in different samples due to the fact that the DLE is a superposition of different contributions from specific defect-related bands [24]. Since the relative concentration of different defect bands can slightly differ between two samples, it is not surprising that there will be a slight shift in the peak center position. These results indicate that the grown ZnO nanorods provided observable emission in the visible region as expected. The emission color of the light from the present diode appears as bluish white. It is important to mention that the hybrid organic–inorganic white-light LED structure discussed above can utilize the different emission possibilities of organic LEDs—e.g. exciton emissions, exciplex emissions—and together with the DLE form the ZnO nanorods.

3.2. Electrical characteristics

Figure 5(a) represents a typical current–voltage (I–V) characteristic for ZnO nanorods/p-SiC heterojunction at RT. The value of the ideality factor was obtained from the slope of the linear region of the semi-logarithmic I–V plot. The ideality factor was found to be in the range 3–4 for all LEDs investigated. The higher value of the ideality factor indicates that the transport mechanism is no longer dominated by the thermo-ionic emission [29]. Non-ideal behavior is often attributed to defect states in the band gap of the semiconductor or at the interface, providing other current transport mechanisms such as structural defects, surface contamination, barrier tunneling or generation recombination in the space charge region, and leading to variations in interface composition [29]. To understand which mechanism dominates junction behavior, the I–V characteristics of the device are studied in a log–log scale.

The log–log plot of the I–V data at RT is shown in the inset of figure 5(a) and it illustrates the current transport mechanism exhibited in three different regions. The current in region I follows a linear dependence, i.e. I–V. This indicates that the current transport is dominated by tunneling at low voltages. The boundary for this region was determined to be below 0.03 V. In region II (0.04–1 V) the current increases exponentially as \(I \sim \exp (cV)\), where \(c\) is a constant. The ideality factor (3–4) is determined in this region and the dominating transport mechanism is recombination-tunneling. Finally, above 1 V the current follows a power law \((I \sim V^2)\), indicating a space-charge limited current transport mechanism. Space-charge limited current (SCLC) and at least one of the other regions observed in the present study have been reported in n-ZnO nanorods/p-Si heterojunctions [30, 31] and in Schottky contact to ZnO nanorods [32].

Figure 5(b) displays the typical I–V characteristics of the ZnO nanorods/p-GaN LED with a 6 V turn-on voltage.

Figures 6(a)–(b) show the I–V characteristics of the two configurations of the organic–inorganic hybrid LED structure discussed above. The corresponding equilibrium energy band diagram of both structures is shown in figures 6(c) and (d). From figures 6(c) and (d), it is clear that there is a significant energy difference between the work function energy level of the PEDOT:PSS (at 5.1 eV) and the HOMO energy level of the organic materials used here. For the NDP-PFO device it is about 0.4, and \(\sim 0.6\) eV for the TFB-PVK case. On the
other hand, the energy barrier for electron injection from the Au to the ZnO layer is relatively large (~ 1.4 eV), and the overall current is expected to be dominated by hole injection from the polymer to the ZnO. The charge flowing in such an organic–inorganic hybrid device is limited by the injection region at low voltage, and at high positive bias it is dominated by SCLC [33, 34]. To overcome the hole injection barrier (0.7 eV) between the PEDOT:PSS and the PFO we have introduced NPD. The NPD will function as hole transport, and in addition to that it will

Figure 5. Typical $I$–$V$ characteristics for (a) $n$-ZnO nanorods/p-SiC LED (LED1), the inset shows the log–log $I$–$V$ data for the same LED, and in (b) $I$–$V$ characteristics in linear scale for the $n$-ZnO/p-GaN (LED2).
act as a barrier dividing layer for holes to facilitate the hopping of holes. The total barrier is divided into two parts, 0.4 eV between the PEDOT:PSS and the NPD, and the remaining 0.3 eV between the NPD and the PFO. This is expected to enhance the total quantity of positive charge inside the device, i.e. a more balanced electron and hole current is expected with a reduced leakage current compared to a PVK-TFB polymer blend LED. As expected, the rectification factor for this device was observed to be 10, (an improvement of about three times compared to the other device). The turn-on voltage for this LED was 4 V and the breakdown voltage was around $-15$ V. On the other hand, the turn-on voltage for the PVK-TFB/ZnO LED was found to be equal to 3 V and the breakdown voltage for this device was $-6$ V. The turn-on voltage here is smaller than for the other device and the reason for this is the reduced number of layers in the devices and hence a reduction in the diode series resistance. Moreover, the rectifying factor for this LED was found to be equal to three.

3.3. Electroluminescence (EL) characteristics

The EL measurements from all fabricated LEDs were carried out using a photo-multiplier detector under dc-bias conditions at RT. The light was collected from the top side of the LEDs. It should be noted that there is no emission under reverse bias, while the broad band visible light EL emission is obvious under forward bias. The corresponding EL spectra for different forward injection currents are shown in figure 7(a). The EL spectra at different currents show three different peaks at 425 nm (violet), 527 nm (green) and 683 nm (red). It is important to mention that due to the three emission lines a bright white light is clearly observed by the naked eye.
eye. These peaks are due to different deep level defects in the ZnO nanorods. Namely, they are due to $V_O$, $V_{Zn}$, oxygen anti-site ($O_{Zn}$), and probably Li. In our EL spectra we have a peak at 2.36 eV (527 nm) which originates from $V_{Zn}$ in the ZnO nanorods [24] and because of which a green light is emitted. The other two peaks (2.9 and 1.8 eV) are also due to two different defects in ZnO nanorods, as mentioned above. Our EL spectra also show that by increasing the current there is no shift in peak positions. We can correlate this EL spectrum with the corresponding PL spectra (figure 3(a)) measured for the same structure. In the PL spectra we have a broad peak extending in the range between 400–700 nm that is the superposition of the different peaks, so that 425, 525 and 683 nm are within this range. The emitted light quality was investigated by measuring the color rendering index and color temperature. The results indicated that the color quality obtained from the ZnO nanorods/p-4H-SiC was of superior quality, with a color rendering index (CRI) of 93 and a color temperature of around 14 000 K. Figures 7(b) and (c) show the color coordinates measurement and a photograph of the ZnO/p-4H-SiC LED under operation, both indicating the superior color quality it is possible to obtain from this LED.

Figure 7. EL spectrum of different LEDs (a) for ZnO nanorods/p-4H-SiC where the ZnO nanorods were grown by the VLS approach, (b) color coordinates measurement of the ZnO nanorod/p-4H-SiC LED, and in (c) and (d) typical photographs (with and without applied voltage) of the bright white light emission obtained from the ZnO/p-4H-SiC LED.
white point was mostly stable with varying current (30–70 mA). Figure 7(b) reveals that the emitted light gives a cold white impression (greenish), with the color coordinates $C_x \approx 0.340$ and $C_y \approx 0.340$ (equivalent to $T = 5657 \text{ K}$).

The EL spectrum of the ZnO nanorods/p-GaN LED consists of two peaks. A blue–violet emission peak at 445 nm that comes from two possible sources is shown in figure 8. This first peak is the transmission from the conduction band to a shallow Mg acceptor and is attributed to p-GaN [35]. The other possible source of this blue–violet emission line is the combination of the zinc interstitial level with the valence band, together with emission due to transmission from the zinc interstitial level to zinc vacancies [36]. The second peak is a broad luminescence band centered at $\sim 535 \text{ nm}$, related to the green band of ZnO that is associated with the conduction band of ZnO to oxygen vacancies, combined with recombination from zinc interstitials to oxygen vacancies [36]. Defect levels at the ZnO/GaN interface influence the recombination radiation spectrum, which results in the increased spectral width of the emission band with its center at 535 nm. The intensities of both emission lines are comparable, thus the superposition of a strong narrow emission line at $\sim 445 \text{ nm}$ and a strong broad emission line at $\sim 535 \text{ nm}$ is responsible for the white-light emission from our LED. The ZnO growth conditions actually are responsible for the state of the defect levels at the ZnO/GaN interface and thus affect the recombination radiation spectrum. Previously, good quality ZnO thin films grown on GaN showed a dominant blue EL band in the spectrum, while thick and amorphous films had a set of several spectral lines [37]. Although we have not yet investigated the color quality of the ZnO nanorods/p-GaN LEDs, a bright, strong, white light color is observed by the naked eye, indicating that two or more colors with high (e.g. blue) and low (e.g green or yellow) energies have been combined.

The EL spectra of the two organic–inorganic hybrid configurations are shown for the NPD/PFO-ZnO nanorods (figure 9(a)), and for the TFB-PVK/ZnO-nanorod LEDs (figure 9(b)). The applied bias condition for the EL spectrum was a clear, visible, bluish-white emission, which began to appear at 16 V. The corresponding current was as low as 0.12 mA for the PFO-NPD/ZnO-nanorod LED, while the corresponding values for the TFB-PVK/ZnO-nanorod LED

**Figure 8.** EL obtained from the ZnO nanorods/p-GaN where the ZnO nanorods were grown by the low-temperature (< 100 °C) ACG approach.
Figure 9. EL of (a) PEDOT:PSS-NPD-PFO/ZnO nanorods LED measured at 18 V and 0.12 mA, and in (b) PEDOT:PSS-PVK-TFB/ZnO nanorods LED measured at 14 V and 0.10 mA, and finally in (c) typical color coordinates characteristics of the PEDOT:PSS-NPD-PFO/ZnO hybrid LED.

were 18 V and 0.10 mA. The EL of the combined polymer-ZnO nanorod hybrid configurations used here yielded an emission with a broad range and three main peaks (figures 9(a) and (b)). The observed emission covers wavelengths ranging from a peak centered at around 455 nm up to a peak centered at 525 nm for both configurations. In figure 9(a) the first sharp high-intensity peak centered at 458 nm belongs to the PFO polymer as described above. The second peak at 524 nm, which lies within the ZnO green emission famous band, is due to Zn-vacancies ($V_{\text{Zn}}$). The third peak centered at 495 nm, observed in both cases (figures 9(a) and (b)), also belongs to the ZnO DLE and originates from oxygen vacancies ($V_{\text{O}}$). Figure 9(b) shows the EL spectrum for the ZnO nanorod/PVK-TFB polymer blend LED; the blue emission at 455 nm corresponds to the PVK polymer material [20] and the other two peaks at 495 nm and 520 nm correspond to emissions within the DLE from ZnO material.
[23, 24]. The color quality was investigated for these organic–inorganic hybrid LEDs. The typical value of the CRI for these hybrid LEDs was approximately 75. Moreover, the color temperature varied from 7500 up to 17 500 K. Figure 9(c) shows a typical color coordinates measurement of ZnO nanorod/PFO hybrid LED. Figure 9(c) reveals that the emitted light has a cold white impression (bluish) with the color coordinates $C_x \approx 0.238$ and $C_y \approx 0.309$ (equivalent to $T = 13 500$ K). Another organic–inorganic structure with the p-type organic polymer placed on top of ZnO nanorods is under investigation. This inverted structure is expected to yield much improved light emission intensity due to the p-polymer layer covering a larger area than in the first structure. A larger pn junction area will in turn reduce the density of the carriers per unit area and hence reduce the non-radiative Auger recombination. Moreover, this inverted polymer (on top)/ZnO nanorod hybrid structure can lead to a reduction of interface surface recombination of the ZnO nanorods studied earlier [38], due to the passivation of the surface by the covering of the ZnO nanorods.

4. Summary

The growth of ZnO nanorods on substrates, including both solid crystalline and soft polymer substrates, is demonstrated. ZnO nanorods with excellent optical emission are demonstrated to have been grown on crystalline as well as amorphous substrates. LEDs utilizing the ZnO nanorods’ broad visible emission combined with different external p-type substrates were fabricated and characterized. The optical and electro-optical characteristics of these LEDs reveal that broad multi-color emission lines can be observed from these diodes, leading to the observation of white light. The color quality obtained from both the ZnO/p-4H-SiC heterojunction and ZnO/p-polymer hybrid LEDs indicates superior light quality with color rendering indexes of approximately 93 and 85, respectively. The EL results presented here indicate that ZnO nanorods with persistent n-type doping can be grown on a variety of p-type substrates and have potential for possible future development of white LEDs. Moreover, the presented white-light organic–inorganic hybrid LEDs with PEDOT:PSS as a contact layer avoid using the otherwise commonly employed ITO, thus reducing the cost associated with the availability of indium, and at the same time providing a ‘green’ electronic solution. These hybrid structures also utilize the emission from organic p-type polymers, with the ZnO nanorods providing a stable electron injector, which is not possible when using purely organic LEDs. Finally, for the inverted hybrid LEDs with top p-polymer layer(s), larger pn junctions with reduced electron density/area can be achieved, leading to a decrease in the non-radiative Auger recombination and an increase in light emission. The preceding arguments imply that ZnO/p-polymer hybrid LEDs obtained on glass or flexible plastic by using low-temperature ACG have potential for the development of future large-area white-light applications.

References

[1] Willander M, Yang L L, Wadeasa A, Ali S U, Asif M H, Zhao Q X and Nur O 2009 J. Mater. Chem. 19 1008–16
[2] Wang Z L and Song J 2006 Science 312 242–5
[3] Sadik P W, Pearton S J, Norton D P, Lambers E and Ren F 2007 J. Appl. Phys. 101 104514

New Journal of Physics 11 (2009) 125020 (http://www.njp.org/)
[4] Willander M, Lozovik Y E, Wadeasa A, Nur O, Semenov A G and Voronova N S 2009 Phys. Status Solidi a 206 853–9
[5] Wagner R S and Ellis W C 1964 Appl. Phys. Lett. 4 89
[6] Zhao Q X, Klason P and Willander M 2007 Appl. Phys. A 88 27–30
[7] Vayssieres L 2003 Adv. Mater. 15 464–6
[8] Yang L L, Zhao Q X and Willander M 2009 J. Alloys Compound. 469 623–9
[9] Klingshirn C 2007 Phys. Status Solidi b 244 3027–73
[10] Ahn H A, Kim Y Y, Kim D C, Mohanta S K and Cho H K 2009 J. Appl. Phys. 105 013502–5
[11] Liu W et al 2006 Appl. Phys. Lett. 88 092101–3
[12] Look D C 2005 Semicond. Sci. Technol. 20 555–61
[13] Claflin B, Look D C, Park S J and Cantwell G 2006 J. Cryst. Growth, 287 16–22
[14] Nadarajah A, Word R C, Meiss J and Konenkamp R 2008 Nano Lett. 8 534–537
[15] Vayssieres L, Kies K, Lindquist S-E and Hagfeldt A 2001 J. Phys. Chem. B 105 3350
[16] Greene L E, Law M, Tan D H, Montano M, Goldberger J, Somorjai G and Yang P 2005 Nano Lett. 5 1231–6
[17] Greene L E, Benjamin D, Yuhas D, Law M, Zitoun D and Yang P 2006 Inorg. Chem. 45 7535
[18] Makinen A J, Hill I G, Shashidhar R, Nikolov N and Kafafi Z H 2001 Appl. Phys. Lett. 79 557–9
[19] Nalwa H S 2001 Handbook of Advanced Electronic and Photonic Materials and Devices vol 10 (San Diego, CA: Academic)
[20] Yu S, Ma C, Cheng C, Wang X, Ji D, Fan Z, Xia D, He W, Chang Y and Du G 2008 Dyes Pigments 76 492–8
[21] Yan H, Huang Q, Scott B J and Marks T J 2004 Appl. Phys. Lett. 84 3873–5
[22] Özgür U, Alivov Ya I, Liu C, Teke A, Reschchikov M, Dogan S, Avrutin V, Cho S-J and Morkoç H 2005 J. Appl. Phys. 98 041301
[23] Klason P, Børseth T M, Zhao Q X, Svensson B G, Kuznetsov A Y, Bergman P J and Willander M 2008 Solid State Commun. 145 321
[24] Børseth T M, Klason P, Zhao Q X, Willander M, Svensson B G and Kuznetsov A Y 2006 Appl. Phys. Lett. 89 262112
[25] Lee K M, Park K H, Koh K H and Lee S 2007 IEEE NEMS'07 2nd IEEE Int. Conf. MPP 5 775–8
[26] Pierce B J and Hengehold R L 1976 J. Appl. Phys. 47 644
[27] Cross R B M, DeSouza M M and Sankara Narayanan E M 2005 Nanotechnology 16 2188–92
[28] Lee S D, Kim Y S, Yi M S, Choi J and Kim S W 2009 J. Phys. Chem. C 113 8954–8958
[29] Allen M W and Durbin S M 2008 Appl. Phys. Lett. 92 12110
[30] Chen X D, Ling C C, Fung S, Beling C D, Mei Y F, Ricky K, Fu Y, Siu G G and Chu P K 2006 Appl. Phys. Lett. 88 132104
[31] Koteeswara Reddy N, Ahsanulhaq Q, Kim J H and Hahn Y B 2008 Appl. Phys. Lett. 92 043127
[32] Klason P, Nur O and Willander M 2008 Nanotechnology 19 475202
[33] Poplavskyy D, Nelson J and Bradley D D C 2003 Appl. Phys. Lett. 83 4–6
[34] So S K, Tsang S W and Tong K L 2006 Org. Electron 7 474–9
[35] Alivov Ya I, Van Nostrand J E, Look D C, Chukichev M V and Ataev B M 2003 Appl. Phys. Lett. 83 14–6
[36] Ahn C H, Kim Y Y, Kim D C, Mohanta S K and Cho H K 2009 J. Appl. Phys. 105 013502
[37] Titkov I E, Zubrilov A S, Delimova L A, Mashovets D V, Linichuk I A and Grekhov I V 2005 Semiconductors 41 564–9
[38] Zhao Q X, Yang L L, Willander M, Sernelius B E and Holtz P O 2008 J. Appl. Phys. 104 073526

New Journal of Physics 11 (2009) 125020 (http://www.njp.org/)