

# Combination of a polyaniline anode and doped charge transport layers for high-efficiency organic light emitting diodes

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Up to now, most organic light emitting diodes (OLEDs) have utilized inorganic materials as transport anodes. In this study, we show that conductive polymers are suitable for this purpose as well. Polyaniline anodes, with a conductivity of 200 S/cm, are used to inject holes into the adjacent organic layers. Due to electrical doping of the electron and hole transport layer with an intrinsic emission layer sandwiched in between (*pin*-OLED), the devices reach high luminance at low voltage. The phosphorescent emitters Ir(MDQ)<sub>2</sub>(acac) and Ir(ppy)<sub>3</sub>, as well as the fluorescent emitter Spiro-DPVBi, are implemented within *pin*-OLEDs using a polyaniline anode. By the use of different host materials, a green double-emitting OLED is demonstrated and compared to the corresponding single emission layer device. Furthermore, a white OLED combining fluorescent and phosphorescent emitting layers is presented, reaching 8.9 lm/W at 1000 cd/m<sup>2</sup>. The results demonstrate an efficient charge carrier injection from the polymer into the *p*-type doped hole transport layer, leading to good power efficiencies of the OLEDs. © 2007 American Institute of Physics. [DOI: 10.1063/1.2748864]

## I. INTRODUCTION

Over the past 20 years, there has been increasing interest in organic light emitting diodes (OLEDs) for color display and lighting applications.<sup>1,2</sup> Usually, these devices use indium tin oxide (ITO) as anode when they are built in the bottom emission form.<sup>3</sup> Often, a polymer layer is spin coated on top of ITO to provide a smooth surface for the following layer stack.<sup>4</sup> Other transparent conducting oxides like fluorine tin oxide or zinc oxide as well as polymer layers were also tested. However, with a few exceptions, neither the roughness nor the work function were sufficient to provide equivalent properties compared to ITO anodes.<sup>5-8</sup>

Efficient electrically doped charge transport layers based on molecular dopants were first demonstrated in 1998.<sup>9,10</sup> OLEDs based on such doped transport layers use an intrinsic emission layer sandwiched in between *p*- and *n*-doped transport layers, which reduce the driving voltage. These so-called *pin*-OLEDs have been demonstrated to have a very high performance and long lifetime.<sup>11,12</sup>

Polyaniline (PANI) is a conductive polymer used for various purposes like printed circuit boards, electrochromic applications, corrosion protection, and transparent conductive coatings.<sup>13</sup> A new dispersion of PANI (D1033) provides a conductivity of 200 S/cm with an extinction coefficient of 0.12 at 750 nm (see Fig. 1). For comparison, the extinction coefficient of ITO is 0.032 at 750 nm, i.e., it is approximately four times lower compared to this PANI dispersion. In contrast, the refractive index of PANI is lower as compared to ITO over the whole visible spectrum, which may lead to an increased light extraction from the organic layers into the glass substrate. In addition, the work function of PANI is around 4.8 eV,<sup>14</sup> which is within the range of the values

reported for plasma treated ITO, namely 4.5–5.11 eV.<sup>15,16</sup> It has been demonstrated that ITO in combination with a *p*-doped transport layer provides a low voltage drop for hole injection. For this reason, the similar work function of PANI is expected to show an efficient charge injection as well.

## II. EXPERIMENT

The polyaniline (D1033) from Ormecon has a solid content of approximately 1% in dispersion and uses water as a solvent. A 100 nm thick polyaniline layer was spin coated (30 s at 1000 rpm on a Delta6RC spin coater) on a glass substrate and afterwards annealed for 1 min at 100 °C in air. For structuring and contacting the OLED, an insulating polystyrene layer was brought onto a part of the coated substrate

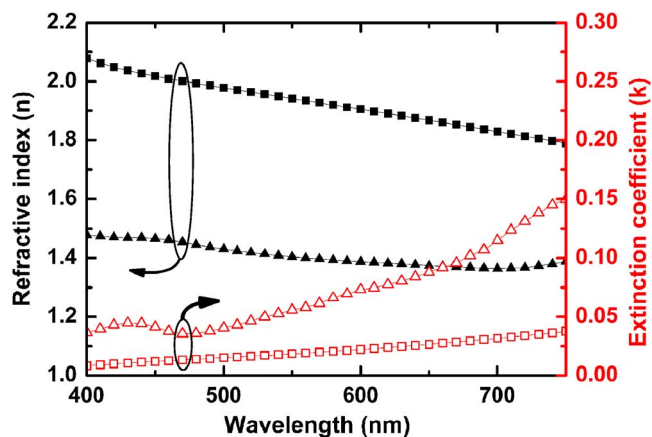


FIG. 1. (Color online) Wavelength dependence of refractive index and extinction coefficient of ITO (squares) and PANI (triangles) films. Both materials show a decrease of refractive index over the whole visible range. For the polymer layer, a local absorption maximum is found at 430 nm, while the extinction coefficient increases toward higher wavelengths up to 0.15 at 750 nm.

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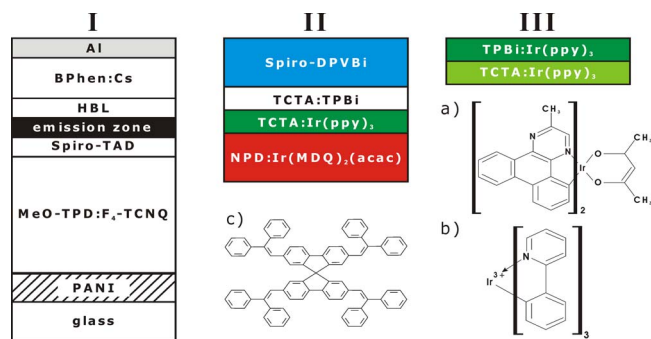


FIG. 2. (Color online) Layer stack of the OLEDs studied in this work. The monochromatic OLEDs differ only in the emission zone (I). For the white OLED, a red (a), green (b), and blue (c) emission layer were stacked with an exciton blocking layer in between the fluorescent and phosphorescent emission zones (II). The charge transport and blocking materials remain unchanged. For each single color device, the thicknesses of the *n*- and *p*-doped charge transport layers were optimized with respect to maximum optical outcoupling. The green D-EML OLED contains two emission layers, both doped with Ir(ppy)<sub>3</sub> (III).

via dip coating. The substrates were annealed a second time for 10 min at 120 °C under nitrogen atmosphere and subsequently loaded into ultrahigh vacuum. N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped with 4 mol % 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>-TCNQ) was evaporated on the PANI-coated substrates. To increase the charge carrier confinement within the emission layer, a 10 nm 2,2',7,7'-tetrakis-(N,N-diphenylamino)-9,9'-spirobifluorene (Spiro-TAD) electron blocking layer was used for all samples. As an emitting layer, either a single emission layer (for monochromatic OLEDs) or a stack of emission layers (for the white or double emission OLED) was used, see Fig. 2. As a hole blocker, 10 nm of 2,2',2''(1,3,5-benzenetriyl) tris-[1-phenyl-1H-benzimidazole] (TPBi) or 4,7-diphenyl-1,10-phenanthroline (BPhen) were used. Cesium was evaporated together with BPhen in a ratio of 1:1 (atom to molecule) acting as electron transport material.<sup>17</sup> The conductivity of both transport layers was in the range of 10<sup>-5</sup> S/cm. Finally, a 100 nm thick aluminum layer was evaporated on top of the organic layers. The OLEDs were measured in the deposition tool, without breaking the vacuum. The current-voltage-luminance characteristics were measured using a Keithley 2400 source measuring unit and a calibrated photodiode (Hamamatsu S7686). Red, green, and blue OLEDs were made, as well as monochromatic devices consisting of a so-called double emission layer (D-EML) and a white OLED. Due to its excellent charge carrier balance, the D-EML is known to reach a very high performance on ITO anodes and was therefore adapted to PANI, using a 6 nm preferably hole conducting emission layer [TCTA:Ir(ppy)<sub>3</sub>] and a following 12 nm thick preferably electron conducting emission layer [TPBi:Ir(ppy)<sub>3</sub>].<sup>11</sup> As the white OLED structure, an approach of Schwartz *et al.* was used which is based on a combination of phosphorescent and fluorescent emitters separated by an exciton blocking layer to prevent triplet exciton quenching.<sup>18</sup> The layer sequence and the layer thicknesses of all devices are given in Table I.

TABLE I. Organic stack layout of the OLEDs discussed in this article. As a hole blocking material, TPBi was used, except of the white OLED, where BPhen served as a hole blocker to keep the comparability to the results published for an ITO anode OLED (see Ref. 18). The doping concentration (in brackets) of the emission layer is given in weight percent.

(nm)	Red	Green	Blue	D-EML	White
PANI	100	100	100	100	100
MeO-TPD:	155	130	145	140	60
F <sub>4</sub> -TCNQ					
SpiroTAD	10	10	10	10	10
Emitter 1	20 (20%)	20 (8%)	10	6 (8%)	20 (5%)
Emitter 2	...	...	...	12 (8%)	2.2 (8%)
TCTA:TPBi	...	...	...	...	2 (2:1)
Emitter 3	...	...	...	...	20
HBL	10	10	10	10	10
BPhen:Cs	65	55	30	45	30
Al			100		

### III. RESULTS

The luminance-voltage characteristics for the red, blue, and green (single and double) emission OLEDs are shown in Fig. 3. As expected, the voltage needed to reach 100 cd/m<sup>2</sup> increases from red (2.72 V) to blue (3.41 V). The D-EML OLED reaches 100 cd/m<sup>2</sup> slightly earlier (at 3.13 V compared to 3.18 V) than the single emission layer (EML) device, which may be explained by an improved charge carrier balance within the emission layer and an expansion of the exciton recombination zone, as described elsewhere.<sup>11</sup> To compare the results of the white OLED to the results of Schwartz *et al.*, BPhen is used as a hole blocking layer (HBL) for the white OLED. BPhen has a lower energy barrier for electron injection compared to TPBi, which is used for all other devices presented here. The lowest unoccupied molecular orbital (LUMO) difference is around 0.3 eV due to LUMOs at 2.7 and 3 eV for TPBi and BPhen, respectively. Thus, 100 cd/m<sup>2</sup> are reached already at 2.87 V although the white OLED contains three emission layers and a thin exciton blocking layer, reaching a total thickness of 44.2 nm intrinsic material instead of ≤20 nm EML for all single color devices. A white OLED with the same structure as

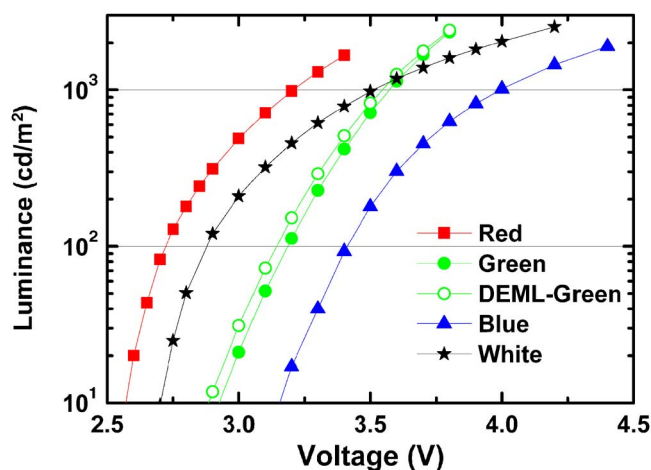


FIG. 3. (Color online) Luminance-voltage characteristics of all OLEDs described in this work using a PANI anode.

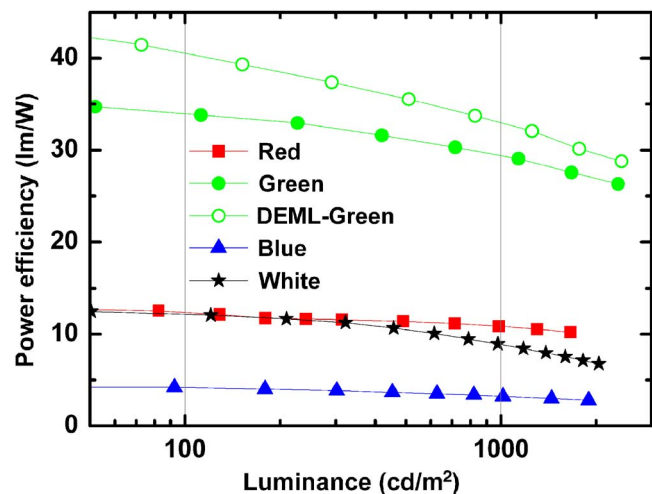


FIG. 4. (Color online) Power efficiency vs luminance curves for the different emitters. Using the improved charge carrier balance of a green D-EML-OLED, the device efficiency is increased from 34 lm/W (single EML) to 40.7 lm/W (D-EML) at 100 cd/m<sup>2</sup>, respectively.

discussed before but with TPBI as HBL, showed almost only blue luminescence due to a strong shift of the charge carrier balance toward a surplus of holes. Thus, the BPhen HBL is needed to provide the charge carrier balance needed for the chosen emission layer setup to obtain white emission.

At 100 cd/m<sup>2</sup>, the single emission layer OLEDs achieve power efficiencies of 12.4, 34, and 4.2 lm/W for the red, green, and blue OLEDs, respectively (Fig. 4). At 100 cd/m<sup>2</sup>, the D-EML green OLED shows an increased power efficiency of 40.7 lm/W. If the phosphorescent green and red EML are combined with the fluorescent blue emitter via the use of an exciton blocking layer,<sup>18</sup> the device emits white light with an efficiency of 12.2 lm/W at 100 cd/m<sup>2</sup>. The spectra of the monochromatic and white OLEDs are depicted in Fig. 5. The white OLED has CIE-1931 color coordinates of (0.42/0.39) which are close to the warm white color point A (0.45/0.41). Thus, the amount of green and blue emission is low compared the contribution of the red emitter. The spectrum of the D-EML green device is nearly identical to its single emission layer counterpart.

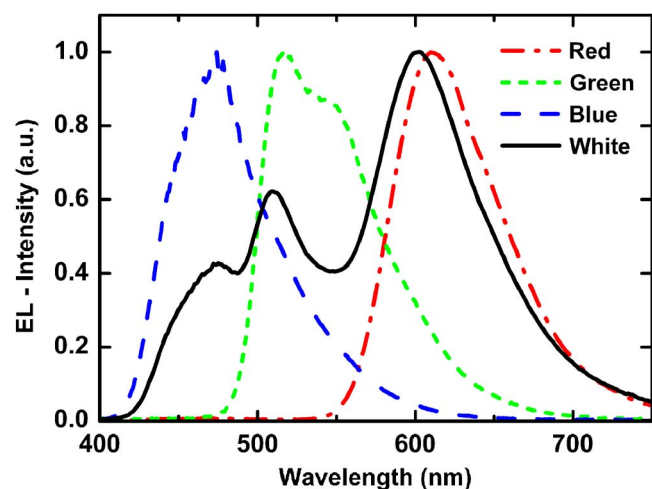


FIG. 5. (Color online) Electroluminescence spectra of the single color OLEDs and their combination in a white OLED.

#### IV. DISCUSSION

All OLEDs on PANI studied in this work show low driving voltages and good efficiencies. The blue *pin*-OLED achieves its maximum current efficiency of 4.6 cd/A at 93 cd/m<sup>2</sup> and 3.4 V, decreasing to 4 cd/A at 1000 cd/m<sup>2</sup>. For the fluorescent emitter Spiro-DPVBi, a current efficiency of 4.2 cd/A (at 2500 cd/m<sup>2</sup>, 10 V) has been reported by Spreitzer *et al.* using a modified KODAK structure on ITO.<sup>19</sup> A comparison of the undoped and *pin*-type OLED structures shows that the use of doped transport layers and thin charge carrier blocking layers leads to a reduced operating voltage and a slightly increased device efficiency for the fluorescent blue emitter. Further on, a *pin*-OLED on ITO with the same materials used for the OLED on PANI, reaches a current efficiency of 4.44 cd/A at 1000 cd/m<sup>2</sup>.

The red OLED on PANI reaches 12.4 lm/W at 2.72 V (100 cd/m<sup>2</sup>) which is decreasing for higher luminance to 10.9 lm/W at 3.2 V (100 cd/m<sup>2</sup>). The same small molecule stack but with an ITO as anode shows a power and current efficiency of 17.3 lm/W and 14.6 cd/A at 100 cd/m<sup>2</sup>. Duan *et al.* demonstrated an ITO-anode OLED with the same emitter, but without doped charge transport layers, which showed a power efficiency of 13.6 lm/W at 6 V.<sup>20</sup> The difference in efficiency between the results from Duan *et al.* and the those reported here can be attributed to the high absorption of PANI in the red spectral region, as well as to different charge blocking layers and to a different host material for the emitter, which leads to a higher current efficiency of 26.6 cd/A (6 V) compared to 10.7 cd/A (100 cd/m<sup>2</sup>, 2.72 V) of our device. However, because of a less efficient charge injection due to undoped charge transport layer in the device of Duan *et al.*, the power efficiency is comparable between both devices.

He *et al.* reported about green single and double emission *pin*-OLEDs with different host and hole blocker materials, reaching power efficiencies of 52 and 77 lm/W at 100 cd/m<sup>2</sup>, respectively.<sup>11,21</sup> With the materials used in this report, we reach on ITO anodes 47.5 and 66.9 lm/W at 100 cd/m<sup>2</sup>, for single and double emission layer OLEDs, respectively. The efficiencies of the green single and double emission OLEDs on PANI obtain values of 34 and 40.7 lm/W at 100 cd/m<sup>2</sup>, respectively. We regard the increased device performance of the D-EML structure compared to the single EML device as an indication for efficient hole injection from the polymer anode into the hole transport layer. In the green D-EML setup, the hole mobility of the TCTA:Ir(ppy)<sub>3</sub> layer is somewhat higher than the electron mobility of TPBi:Ir(ppy)<sub>3</sub>. Therefore, the ratio between the layer thicknesses is chosen to compensate this mobility difference. Consequently, the main exciton generation zone is close to the interface of both layers. Since there is a partial interpenetration of charge carriers, the overall exciton recombination zone is widened.<sup>11</sup> An unbalanced electron/hole ratio, resulting from a less efficient hole injection in the case of the PANI anode, would therefore cause a shift of the exciton generation zone toward the electron blocking layer and, thus, result in lower or at best unchanged device performance compared to the single emission layer device.<sup>22</sup> Since the

gain in device efficiency by changing the device structure from a single to the double emission layer is 20% for PANI, compared to 41% for ITO devices with the same small molecule materials, a slightly different charge carrier balance can be expected in the case of the polymer anode.<sup>11,21</sup>

A white OLED serves as another test for the hole injection from PANI into the hole transport layer: The white OLED stack, depicted in Fig. 2 (I and II), is very sensitive to the charge carrier balance within the EML. The OLED structure was developed by Schwartz *et al.* for a white OLED on an ITO anode.<sup>18</sup> Using PANI instead of ITO, only minor differences in the spectra are found: The CIE coordinates of the ITO and PANI anode devices are (0.47/0.42) and (0.42/0.39), respectively. Because of the higher fraction of blue light in the spectrum and the higher extinction coefficient of the PANI anode, the white OLED on PANI reaches a power efficiency of 8.9 lm/W at 1000 cd/m<sup>2</sup>, which is lower than the 13.7 lm/W reached by the same white OLED on ITO.

When evaluating the low driving voltage of all PANI anode OLEDs and their efficiencies, one can expect a good hole injection at the PANI/MeO-TPD:F<sub>4</sub>-TCNQ interface. Since the same transport layer and emitter stack of the white OLED as in the device of Schwartz *et al.* are used, a different charge carrier balance and the high extinction coefficient of PANI in the red may explain the different spectra. A less efficient hole injection would cause an increased ratio of electrons to holes within the white OLED emission zone, corresponding to a shift of the exciton generation zone toward the red and green EML and, thus, a higher amount of green and red light would occur.<sup>22</sup> For a warm white spectrum, the red emitter has the largest contribution to the spectrum. Consequentially, the efficiency of the red emitter is contributing significantly to the overall device efficiency. However, in the case of PANI, the anode has its absorption maximum just in the emission region of the red emitter, which causes a decrease of the OLED efficiency and a reduced ratio of red as compared to green and blue light in the spectrum. Overall, we observe that the efficiency of the white, green, and red OLEDs with PANI anode is lower than on ITO, which may be explained by the higher absorption of PANI in the visible part of the spectrum (Fig. 1) and its lower conductivity as compared to ITO. However, our results show that PANI could replace inorganic anodes in OLEDs, especially when the absorption in the visible part of the spectrum can be further reduced.

## V. CONCLUSION

We demonstrated efficient *pin*-OLEDs on a polyaniline anode without using a transparent conducting oxide layer underneath. At 100 cd/m<sup>2</sup>, the red, green, and blue OLEDs achieved power efficiencies of 12.4, 34, and 4.2 lm/W, re-

spectively. We further demonstrated an efficiency enhancement by the use of a green double emission layer structure to achieve 40.7 lm/W at a luminance of 100 cd/m<sup>2</sup>. By combining phosphorescent and fluorescent emitters, a white OLED is shown with 12.2 lm/W and CIE coordinates of (0.42/0.39) at 100 cd/m<sup>2</sup>, closely corresponding to the warm-white color point A. The results show that the use of *p*-doped charge transport layers allows an efficient hole injection from polyaniline into the adjacent small-molecule OLED stack, while at the same time only low driving voltages are needed. Double emission layer OLEDs and white OLED structures on a polyaniline anode, serving as test vehicles for studying the charge carrier balance, indicate a similar charge carrier balance within the emission zone as in ITO-based OLEDs.

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<sup>1</sup>C.-J. Yang, C.-L. Lin, C.-C. Wu, Y.-H. Yeh, C.-C. Cheng, Y.-H. Kuo, and T.-H. Chen, *Appl. Phys. Lett.* **87**, 143507 (2005).

<sup>2</sup>M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).

<sup>3</sup>C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).

<sup>4</sup>Ch. Jonda, A. B. R. Mayer, U. Stolz, A. Elschner, and A. Karbach, *J. Mater. Sci.* **35**, 5645 (2000).

<sup>5</sup>Y. Tomita, C. May, M. Törker, J. Amelung, K. Leo, K. Walzer, K. Fehse, and Q. Huang, *Proc. of Org. El. Conf.*, P020410, 2006.

<sup>6</sup>O. Kluth, G. Schöpe, J. Hüpkes, C. Agashe, J. Müller, and B. Rech, *Thin Solid Films* **442**, 80 (2003).

<sup>7</sup>X. Jiang, F. L. Wong, M. K. Fung, and S. T. Lee, *Appl. Phys. Lett.* **83**, 1875 (2003).

<sup>8</sup>A. Andersson, N. Johansson, P. Bröms, N. Yu, D. Lupo, and W. R. Salaneck, *Adv. Mater.* **10**, 859 (1998).

<sup>9</sup>J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **73**, 729 (1998).

<sup>10</sup>M. Pfeiffer, A. Beyer, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **73**, 3202 (1998).

<sup>11</sup>G. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, and J. Salbeck, *Appl. Phys. Lett.* **85**, 3911 (2004).

<sup>12</sup>R. Meerheim, K. Walzer, M. Pfeiffer, and K. Leo, *Appl. Phys. Lett.* **89**, 061111 (2006).

<sup>13</sup>B. Wessling, *Synth. Met.* **93**, 143 (1998).

<sup>14</sup>B. Zeysing, Ormecon GmbH, personal communication.

<sup>15</sup>D. J. Milliron, I. G. Hill, C. Shen, A. Kahn, and J. Schwartz, *J. Appl. Phys.* **87**, 572 (2000).

<sup>16</sup>J. H. Choi, E. S. Lee, S. H. Choi, H. K. Baik, K. M. Song, and Y. S. Lim, *J. Vac. Sci. Technol. A* **23**, 1479 (2005).

<sup>17</sup>J. Huang, J. Blochwitz-Nimoth, M. Pfeiffer, and K. Leo, *J. Appl. Phys.* **93**, 838 (2003).

<sup>18</sup>G. Schwartz, K. Fehse, M. Pfeiffer, K. Walzer, and K. Leo, *Appl. Phys. Lett.* **89**, 083509 (2006).

<sup>19</sup>H. Spreitzer, H. Schenk, J. Salbeck, F. Weissoertel, H. Riel, and W. Ries, *Proc. SPIE* **3797**, 316 (1999).

<sup>20</sup>J.-P. Duan, P.-P. Sun, and C.-H. Cheng, *Adv. Mater.* **15**, 224 (2003).

<sup>21</sup>G. He, O. Schneider, D. Qin, X. Zhou, M. Pfeiffer, and K. Leo, *J. Appl. Phys.* **95**, 5773 (2004).

<sup>22</sup>B. Y. Lee, *Appl. Phys. Lett.* **89**, 153503 (2006).