High-brightness II–VI light-emitting diodes grown by molecular-beam epitaxy on ZnSe substrates

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High-brightness blue and green light-emitting diodes (LEDs) based on II–VI double heterostructures (DHs) have been successfully grown by molecular-beam epitaxy (MBE) on (100) ZnSe substrates. These LED structures consist of a 500–1000 Å thick active region of undoped blue-emitting Zn$_{0.9}$Cd$_{0.1}$Se/ZnSe multiple quantum wells or a green-emitting ZnTe$_{0.3}$Se$_{0.7}$ single quantum well sandwiched between a 2–3 μm thick n-type ZnSe:Cl layer and a ~1 μm thick p-type ZnSe:N layer. Operated at 10 mA (3.0 V), the blue LEDs produce 327 μW of light output sharply peaked at 489 nm, corresponding to an external quantum efficiency of 1.3%. The green LEDs generate 1.3 mW of light peaked at 512 nm with a corresponding external quantum efficiency of 5.3%. In terms of photometric units, the luminous efficiencies for these II–VI blue and green LEDs are 1.7 and 18.0 lm/W, respectively. © 1995 American Vacuum Society.

I. INTRODUCTION

High-brightness blue and green LEDs (light-emitting diodes) are highly desirable for numerous practical applications such as multicolor LED indicators, traffic control signals, and full-color large-area flat-panel displays. Wide band gap II–VI semiconductor compounds have been regarded as very promising materials for the fabrication of both LEDs and laser diodes. Enormous progress has been achieved in the development of ZnSe-based II–VI blue/green light emitters in recent years. In the work to date, practically all of the ZnSe-based devices have been grown on GaAs substrates. This is not only because GaAs has a very small lattice mismatch (0.27%) to ZnSe at room temperature, but also due to the fact that large-area high quality (including epi-ready) GaAs substrates are commercially available. In addition, GaAs surface preparation techniques for molecular-beam epitaxy (MBE) film growth are well established. By adding ~7% sulfur into the ZnSe lattice to form the ternary alloy ZnS$_{0.07}$Se$_{0.93}$, an exact lattice match to GaAs at typical growth temperatures (220–320 °C) can be achieved. However, due to the fairly large difference in thermal expansion coefficients between GaAs and ZnS$_{0.07}$Se$_{0.93}$, a tensile strain at the heterointerface exists at room temperature even when the ZnS$_{0.07}$Se$_{0.93}$ epilayer is exactly lattice matched to the GaAs substrate at the growth temperature. This is confirmed by and frequently observed as a large angular separation (~200 arc s) between the (400) x-ray diffraction peaks of the GaAs substrate and the ZnS$_{0.07}$Se$_{0.93}$ epilayer at room temperature. This interfacial strain, along with the accompanying stacking faults and dislocation defects provide the seed for the formation and growth of dark-line defects (DLDs) which are believed to be the principal degradation source which limits the useful lifetime of the current II–VI LEDs and laser diodes. Moreover, interdiffusion effects in the II–VI/II–V heterointerface can cause imperfect nucleation which can give rise to a high density of interfacial and threading dislocations that also adversely affect device lifetime. In addition, from a device point of view, the opaque GaAs substrate limits the maximum light extraction efficiency of a blue/green LED due to absorption of the light which is emitted toward the substrate from the active region of the device. In principle, utilization of a transparent substrate rather than an opaque substrate may be expected to increase the optical efficiency of II–VI blue/green LEDs by a factor of five. To overcome the above-mentioned difficulties, an obvious approach is to use ZnSe substrates for the growth of ZnSe-based devices. Unfortunately, due to the general unavailability of high quality ZnSe substrates, only a few efforts to grow homoepitaxial ZnSe thin films and devices have been reported to date. Recently, however, significant improvement in the growth of large-area single-crystalline bulk ZnSe using a seeded physical vapor transport (SPVT™) technique developed at Eagle-Picher Research Laboratory has been demonstrated. In this article, we report the first high-brightness II–VI blue and green LEDs grown by MBE (molecular beam epitaxy) on Eagle–Picher (100) ZnSe substrates.

II. EXPERIMENTAL DETAILS

The II–VI LED heterostructures were grown on (100) ZnSe substrates produced at Eagle–Picher Research Laboratory by the SPVT™ process. The ZnSe wafers were cut from oriented 50 mm diameter by ~25 mm thick single-crystal ZnSe ingots. The ZnSe wafers are twin-free and contain no small-angle grain boundaries. Etch pit densities range from 2–5×10$^4$ cm$^{-2}$. To prepare the ZnSe substrates for epitaxy, proprietary polishing techniques were employed to remove the processing damage and to produce an atomically flat substrate surface. The crystalline quality of the substrates was evaluated using the double-crystal x-ray diffraction technique. Typical full-width at half-maximum (FWHM) of the...
(400) diffraction peak from these ZnSe substrates range from 11–16 arc s, indicating that the ZnSe crystal quality is comparable to that of GaAs.

The MBE growth experiments were carried out at North Carolina State University (NCSU). Prior to each film growth, a preheat procedure was employed to remove unwanted contaminants on the ZnSe substrate surface. Reflection high-energy electron diffraction (RHEED) was used to monitor the substrate surface during preheat and initial ZnSe film nucleation. It should be noted that, even before the thermal preheat, the polished ZnSe substrates exhibited a streaky RHEED pattern at room temperature. This elongated (2×1) surface reconstruction RHEED pattern was clearly visible at the onset of the preheat cycle and became brighter when the substrate was heated to ≈440 °C for 5 min in the MBE chamber. Auger spectra of the ZnSe substrate surface before and after this preheat procedure, as shown in Fig. 1, indicate that unwanted surface contaminants such as C, O, and Cl were successfully removed.

ZnSe-based blue and green p-on-n DHs were grown by MBE on (100) ZnSe substrates at 275 °C. A solid ZnCl2 source and an rf nitrogen plasma source were used to provide n-type and p-type dopants, respectively. As shown schematically in Fig. 2, the LED heterostructures consist of a 500–1000 Å thick active region sandwiched between a 2–3 μm thick n-type ZnSe:Cl layer and a ~1 μm thick p-type ZnSe:N layer. A Zn0.9Cd0.1Se (~100 Å)/ZnSe (~50 Å) MQW (five wells) structure and a 500–1000 Å thick ZnTe0.1Se0.9 quantum well were employed as active regions in the blue and green device structures, respectively, as shown in Fig. 2. Thin (~200 Å) HgSe/ZnTeSe epilayers were grown by MBE to form better ohmic contact to the top p-type ZnSe:N layer. Additional details of the MBE growth procedures have been published earlier.

Conventional photolithographic and etching techniques were used to fabricate 250 μm×250 μm mesa structures. Gold was evaporated onto the top HgSe layer to form 100 μm×100 μm electrode pads. Indium metal contact to the top of the etched n-type ZnSe:Cl epilayer, as shown in Fig. 2, was necessary due to the insulating nature of current ZnSe substrates. Excellent current–voltage (I–V) characteristics were obtained by using the HgSe/ZnTeSe contacting scheme.
Typically, as demonstrated in Fig. 2(c), a current of 10 mA flowing through the device requires a forward bias of only 3.00 V. For testing and demonstration purposes, the processed LED chips were packaged in an industrial standard T-1 3/4 clear-epoxy lamp configuration. The light emission from the LEDs was collected using a calibrated integrating sphere and a 256-element Si photodiode array, along with a computer and necessary software.

III. RESULTS AND DISCUSSION

Double-crystal x-ray diffusion studies of the blue and green LED heterostructures yielded FWHM of ~400 peaks as narrow as 22 arc s, as shown in Fig. 3. We believe this is the narrowest x-ray rocking curve ever reported for a II–VI blue/green light emitter and is an indication of the high crystalline quality of the substrate/device structure. Figure 4 shows the optical output spectra for representative II–VI blue and green LEDs. The emission spectra of blue and green LEDs based on GaN/InGaN heterostructures obtained from Nichia Chemical Industries, Japan are also included for comparison. Figure 4(a) shows the light output from a ZnCdSe blue LED which is sharply peaked at 489 nm with a FWHM = 83 meV. The LED produces 327 µW of light output at 10 mA drive current, corresponding to an external quantum efficiency of 1.3%. This is approximately 40 times brighter than commercial SiC LEDs and is the brightest blue LED ever made from II–VI semiconductor materials (see Table I). For comparison, Fig. 4(b) shows the light output spectrum from a Nichia InGaN blue LED, measured at NCSU, this impressive device produces 1.04 mW at 10 mA and exhibits an external quantum efficiency of 3.8%. However, the nitride-based LED has a very broad emission spectrum (FWHM=481 meV) that spans from the violet to the yellow-orange spectral region and, consequently, makes the light output appear whitish-blue to the eye.

The emission spectrum for a ZnTeSe green LED is shown in Fig. 4(c). Operated at 10 mA, the device produces 1.3 mW peaks at 512 nm, corresponding to an external quantum efficiency of 5.3%. The ZnTeSe green LEDs reported here are the brightest green LEDs ever made from any semiconductor material. Their external quantum efficiency is more than 50 times higher than that of GaP LEDs which produce light output peaked in the yellow–green spectral region at 555 nm (see Table I). Although the presence of Te broadens the emission somewhat (FWHM=234 meV) since Te acts as an isoelectronic hole trap, most of the light output from the
ZnTeSe LEDs falls into the blue–green to green spectral region from 500–550 nm. As a result, the light emission from these LEDs appears as pure-green to the eye. Measured at NCSU, the emission spectrum for a Nichia green LED is shown in Fig. 4(d) for comparison. This device produces 635 μW peaked at 514 nm, which corresponds to an external quantum efficiency of 2.6%. Once again, the emission is quite broad (FWHM=485 meV) so that the light appears whitish–green to the eye.

An important key issue concerning the development of II–VI blue/green light emitters which remains to be addressed is that of device reliability. All of the II–VI light emitters produced to date suffer from degradation of their light output with time.\(^{15–17}\) In the case of laser diodes, the longest published cw lifetime at room temperature so far is about 9 min.\(^{18}\) The homoepitaxial growth approach using ZnSe substrates instead of GaAs has resulted in improved lifetimes for LEDs fabricated at NCSU. Figure 5 shows at room temperature degradation of two ZnTeSe green LEDs operated continuously at two different dc current densities. The observed decrease in optical power output \(P(t)\) as a function of operating time \(t\) follows the equation

\[
P(t) = P_0 \exp\left(-\frac{t}{\tau}\right),
\]

where \(P_0\) is the initial optical power output at \(t=0\) and \(\tau\) is the exponential lifetime of the device.\(^{19}\) As shown in Fig. 5, for an operating current density of 15 A/cm\(^2\), \(\tau=675\) h. For a higher current density of 50 A/cm\(^2\), \(\tau=350\) h. The data indicate that an increase of the current density flowing through the LED accelerates the device degradation process. Similar behavior is found for LEDs composed of III–V materials and has been attributed to the growth of point defects within the active region of the device.\(^{19}\) Additional studies are underway at NCSU to clarify the microscopic basis of the observed exponential degradation in ZnSe-based light emitters. Preliminary x-ray diffraction and transmission electron microscopy (TEM) studies indicated that the dislocation densities in current devices grown on ZnSe substrates are approximately \(10^6\) per cm\(^2\). Improvements in nucleation and growth are expected to reduce dislocation densities and thus increase the II–VI device lifetime significantly in the near future. We estimate that defect densities must be reduced to \(10^5\) per cm\(^2\) or less for II–VI optoelectronic devices to be commercially viable.

### IV. SUMMARY

In summary, high-brightness, high-efficiency blue and green LEDs based on II–VI DHs have been successfully grown by MBE on ZnSe substrates. These devices have been processed, packaged and tested. The blue LEDs employ a Zn\(_{0.9}\)Cd\(_{0.1}\)Se/ZnSe MQW active region and produce 327 μW at 10 mA with the light output peaked at 489 nm, corresponding to an external quantum efficiency of 1.3%. The green LEDs employ a ZnTe\(_{0.1}\)Se\(_{0.9}\) active region and generate 1.3 mW at 10 mA peaked at 512 nm, corresponding to an external quantum efficiency of 5.3%. In terms of photometric units, the luminous efficiencies of the blue and green LEDs are 1.7 and 18.0 lm/W, respectively, when operated at 10 mA (3.0 V).

### ACKNOWLEDGMENTS

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**TABLE I. Comparison of physical properties of blue and green LEDs.**

<table>
<thead>
<tr>
<th>LED active region</th>
<th>Peak (nm)</th>
<th>Power (μW) (@10 mA)</th>
<th>(\eta_{\text{ext}}) (%)</th>
<th>(\eta_{\text{int}}) (%)</th>
<th>(\eta_{\text{pow}}) (%)</th>
<th>(\eta_{\text{LMW}}) (lm/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>555</td>
<td>26</td>
<td>0.1</td>
<td>1.8</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>InGaN</td>
<td>514</td>
<td>635</td>
<td>2.6</td>
<td>10</td>
<td>2.0</td>
<td>7.3</td>
</tr>
<tr>
<td>ZnTeSe</td>
<td>512</td>
<td>1300</td>
<td>5.3</td>
<td>28</td>
<td>4.3</td>
<td>18.0</td>
</tr>
<tr>
<td>ZnCdSe</td>
<td>489</td>
<td>327</td>
<td>1.3</td>
<td>7</td>
<td>1.1</td>
<td>1.7</td>
</tr>
<tr>
<td>SiC</td>
<td>470</td>
<td>11</td>
<td>0.04</td>
<td>0.9</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>InGaN(^b)</td>
<td>450</td>
<td>1040</td>
<td>3.8</td>
<td>15</td>
<td>3.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> \(\eta_{\text{ext}}\)—external quantum efficiency, \(\eta_{\text{int}}\)—internal quantum efficiency, \(\eta_{\text{pow}}\)—external power efficiency, and \(\eta_{\text{LMW}}\)—external luminous efficiency. See Ref. 3 for a discussion of above efficiencies.

<sup>b</sup>Reference 17.
Yu et al.: High-brightness II–VI LEDs


