Blue-Green Light-Emitting Diodes and Lasers Based on Wide-Band-Gap II-VI Materials

J. F. Schetzina

North Carolina State University
Office of Sponsored Programs
Box 7514
Raleigh, NC 27695-7514

Department of the Navy
Office of Naval Research
Atlanta Regional Office
101 Marietta Tower
Atlanta, GA 30323-0008

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The objective of this research program is the development of the wide-band-gap II-VI material ZnSe, along with the related alloys ZnCdSe, for use in applications which require efficient and long-lived blue/green light emitting diodes (LEDs) and laser diodes (LDs).
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J.F. Schetzina, Principal Investigator

FINAL REPORT

A. SUMMARY OF PROGRAM RESULTS

IMPORTANT ADVANCES IN BULK ZnSe CRYSTAL GROWTH

Eagle-Picher Laboratory personnel, under the direction of Gene Cantwell, have recently succeeded in reproducibly preparing doped (n-type) ZnSe bulk crystals. By varying the doping parameters, it is now possible for Eagle-Picher scientists to selectively dope ZnSe bulk crystals with carrier concentrations in the range $10^{17}$ cm$^{-3}$ to nearly $10^{18}$ cm$^{-3}$. This is illustrated by the Hall effect data shown in Figure 4. Figure 4(a) shows plots of carrier concentration and mobility versus temperature for a ZnSe wafer doped to $10^{17}$ cm$^{-3}$ at room temperature. It is seen that the crystal displays excellent mobilities ranging from about 400 cm$^2$/V-s at 300 K to nearly 800 cm$^2$/V-s at lower temperatures. This is comparable to the best electron mobilities achieved for ZnSe films grown by MBE at this doping level. Figures 4(b) and 4(c) show comparable data for more heavily doped wafers. It is seen from Figure 4(c) that an electron doping level of $8 \times 10^{17}$ per cm$^3$ for bulk n-type ZnSe has been achieved. The data indicate that this corresponds to degenerately-doped ZnSe. This result is extremely significant: The development of highly-conducting ZnSe bulk crystals by Eagle-Picher means that laser diode structures, as well as efficient LEDs, can now be grown and processed on Eagle-Picher ZnSe substrates.

X-ray topography experiments have also been completed at the NIST facility in Gaithersburg, Maryland on Eagle-Picher ZnSe wafers. Specifically, transmission topography experiments have been completed to measure directly the dislocation

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density in the ZnSe wafers. Initial experiments in 1993 showed a dislocation density of more than $10^4$ per cm$^2$. However, due to improvements in ZnSe crystal growth and surface preparation at Eagle-Picher Laboratories, the most recent ZnSe wafers investigated by transmission topography at NIST show dislocation densities as low as 640 per cm$^2$. This remarkable result is shown in the X-ray transmission topograph image shown in Figure 5. The topograph image is for a total area of 5.48 mm$^2$. The black marks are dislocation counting marks that were added to the photograph by NIST personnel. The total number of dislocations in the photo is 35, which corresponds to a dislocation density of 6.4 per mm$^2$ or only 640 dislocations per cm$^2$. This is comparable to dislocation densities in the highest quality GaAs substrates that are currently available, and is well below the $10^4$ per cm$^2$ dislocation density that has been estimated as a necessary condition for long-lived II-VI optoelectronic devices.
Figure 4. Electrical properties of n-type substitutionally doped bulk ZnSe.
Figure 5. X-ray topography of ZnSe wafer. Only thirty-five dislocations are seen (black marks), corresponding to a wafer dislocation density of 640 per cm$^2$ (work performed at NIST Laboratories, Gaithersberg, MD).
The ONR program funded by ONR grant N00014-92-J-1644, J.F. Schetzina, Principal Investigator, May 1, 1992 - October 31, 1994) initiated a study of homoeptaxial growth of wide band gap II-VI materials on ZnSe substrates. The goal of this initial 30 month program was to demonstrate the viability of growth of LED and laser diode structures on ZnSe substrates as compared with heteroepitaxial growth of II-VI structures on GaAs substrates. Other key issues that were to be addressed included p-type doping of ZnSe using nitrogen plasma sources and the ohmic contact problem for p-type ZnSe. We can report substantial success in achieving all of the above program goals. Following is a listing of the principal accomplishments of the program:

1. **Commercial grade ohmic contacts for p-type ZnSe.** Under the current program, NCSU has developed excellent ohmic contacts for p-type ZnSe based on HgSe/ZnTeSe epitaxial layers which minimize the band offset [1-4]. Currently, at NCSU, light emitting diodes are routinely fabricated which produce 20 mA at 3.2 V using the above homoeptaxial contacting scheme. This ohmic contacting scheme forms the basis of integrated heterostructure devices for blue/green light emission applications. NCSU was awarded U.S. patent no. 5,294,833 entitled "Integrated Heterostructure of Group II-VI Semiconductor Materials Including Epitaxial Ohmic Contact and Method of Fabricating Same", which describes a variety of LED and laser diode structures equipped with HgSe/ZnTeSe contacts which are covered by the patent.

2. **A comprehensive study of the light emission from nitrogen plasmas generated in an Oxford Applied Research rf plasma source and an ASTeX ECR source was successfully completed.** The results of this study, which were reported in three scientific papers [5-7] during the course of the present program, provided that first direct experimental evidence that these sources generate an appreciable flux of nitrogen atoms. The nitrogen atoms are now believed to be the species of nitrogen
that is most likely responsible for the p-type doping of ZnSe and related alloys. On the basis of these studies, we have been able to optimize the p-type doping of ZnSe and related alloys. Present doping levels of ZnSe at NCSU exceed 1018 cm⁻³ free holes at room temperature — the highest p-type doping level achieved in the entire world.

3. A detailed study of the surface of ZnSe substrate wafers supplied by Eagle-Picher Industries has been completed using Auger spectroscopy. The results of this study [8] showed that the, as polished surface of ZnSe was heavily contaminated by both oxygen (thought to be bound to Zn) and carbon. Detailed studies via Auger spectroscopy of the effects of a variety of chemicals used for degreasing (trichloroethylene, acetone, methanol) and for chemical etching (various acids, bromine-methanol, etc.) of ZnSe were completed. Working closely with Eagle-Picher personnel, we have recently improved, in a very significant way, the surface preparation of ZnSe. As a consequence, we at NCSU are now the only MBE group in the world able to prepare high quality ZnSe films and device structures on ZnSe substrates.

4. High-brightness light-emitting diodes (LEDs) operating at peak wavelengths in the blue (486-489 nm) and in the pure green (508-514 nm) spectral regions have been successfully synthesized, processed, and tested [9,10]. The II-VI double-heterostructure (DH) devices were grown by molecular beam epitaxy (MBE) at North Carolina State University (NCSU) using (100) ZnSe substrates produced at Eagle-Picher Laboratory by the Seeded Physical Vapor Transport (SPVT™) process [11,12]. Substrate wafers were cut from oriented 50 mm diameter by ~25 mm thick single-crystalline ZnSe ingots. The ZnSe wafers are twin-free and contain no small-angle grain boundaries. Double-crystal x-ray diffraction rocking curve studies yield FWHM (400) = 11-16 arc sec, indicating ZnSe crystal quality comparable to that of GaAs substrates.
The blue and green LED device structures (Fig. 1) consist of a 2-3 μm thick layer of n-type ZnSe:Cl, a 500-1,000 Å thick active region, and a 1.0 μm thick p-type ZnSe:N layer. For the blue LED (Fig. 1(a)), the active region consists of five 100 Å Zn$_{0.9}$Cd$_{0.1}$Se quantum wells separated by four 50 Å ZnSe barrier layers. The active region of the green LED (Fig. 1(b)) consists of a single 1000 Å layer of ZnTe$_{0.1}$Se$_{0.9}$. Thin (~100 Å) epitaxial surface layers of HgSe/ZnTeSe were deposited by MBE to obtain better ohmic contact to the top p-type ZnSe layer. MBE growth details are discussed in previous publications [13,14].

Standard photolithographic and etching techniques [13,14] were used to fabricate 250 μm x 250 μm mesa diode structures. Gold (100 μm x 100 μm) was used as a metal contact to the top HgSe layer of each device; indium was used to contact the n-type ZnSe layer. Direct contact to the n-type ZnSe epilayer was necessitated because of the insulating nature of current ZnSe substrates. The HgSe/ZnTeSe contacting scheme produced an excellent ohmic contact, as is evidenced by the current-voltage (I-V) curve for a processed LED shown in Fig. 1(c).

The LEDs were packaged in a standard T-1 3/4 clear-epoxy lamp configuration for testing. The optical properties of the devices were measured using a Photo Research SpectraScan system which consists of a model PR-704 spectroradiometer equipped with a 256-element silicon photodiode array that is thermoelectrically-cooled.
Figure 1. (a) Blue LED structure, (b) green LED structure, and (c) I-V characteristics for processed device.
to 0 °C for maximum sensitivity and efficiency, a model IS-701A/703A calibrated integrating sphere, and SpectaView computer software for measuring LED properties in both radiometric and photometric units. In radiometric units, the total LED output power or radiant flux $\Phi_e$ (in watts) is first measured. The external quantum efficiency $\eta_{q_{\text{ext}}}$ is obtained by dividing the measured radiant flux $\Phi_e$ from the device by the photon energy (in eV) of the peak emission $E_{\text{ph}}$, and then dividing this number by the current $I$ (in amperes) flowing through the device [15]:

$$\eta_{q_{\text{ext}}} = \frac{\Phi_e}{I \cdot E_{\text{ph}}} \text{ (photons/electron).} \quad (1)$$

The external power efficiency $\eta_{p_{\text{ext}}}$ is obtained by dividing the measured radiant flux from the LED by the product of the current $I$ times the applied voltage $V_{\text{app}}$ [15]:

$$\eta_{p_{\text{ext}}} = \frac{\Phi_e}{I \cdot V_{\text{app}}} \text{.} \quad (2)$$

Finally, the luminous performance (sometimes called the luminous efficiency) $\eta_{v_{\text{ext}}}$ of the LED is obtained from the measured luminous flux $\Phi_v$ (in lumens) by dividing this quantity by the product of the current $I$ times the applied voltage $V_{\text{app}}$ [15]:

$$\eta_{v_{\text{ext}}} = \frac{\Phi_v}{I \cdot V_{\text{app}}} \text{ (lumens/watt).} \quad (3)$$

Figure 4 shows plots of the light emission versus wavelength for representative blue and green LEDs based on II-VI heterostructures. The emission characteristics of an InGaN blue LED from Nichia Chemical Industries (Japan) is also shown for comparison. Fig. 4(a) shows that the light output from the ZnCdSe blue LED is sharply peaked at 489 nm with a full-width-at-half-maximum (FWHM) of 72 meV. The ZnCdSe device produces 327 $\mu$W at 10 mA, corresponding to an external quantum efficiency $\eta_{q_{\text{ext}}} = 1.3\%$. This is approximately 30 times larger than commercial SiC LEDs and is the brightest blue LED ever made from II-VI materials.
Figure 2. Light output characteristics for (a) blue ZnSe/ZnCdSe LED, (b) blue GaN/InGaN LED (Nichia Chemical), and (c) green ZnSe/ZnTeSe LED.
For comparison, Fig. 4(b) shows the emission spectrum for a Nichia Chemical Industries blue LED based on InGaN [6]. The InGaN device produces 1.04 mW at 10 mA and exhibits an external quantum efficiency of $\eta_{q_{\text{ext}}}=3.8\%$. These are extremely impressive characteristics. Note, however, that the InGaN LED produces a very broad emission spectrum (FWHM = 510 meV) with the light output spanning from the violet to the yellow-orange spectral region. This broad spectrum, which results from the intentional introduction of Zn into the InGaN active region of the device to produce a deep-level emission peaked at ~450 nm [16], makes the output appear whitish-blue when the LED is viewed with the human eye.

Figure 4(c) shows the optical emission spectrum for a ZnTeSe green LED. The ZnTeSe device produces 1.3 mW at 10 mA, corresponding to an external quantum efficiency of $\eta_{q_{\text{ext}}}=5.3\%$. The ZnTeSe green LEDs which we are reporting represent the brightest green LEDs ever made from any semiconductor material. They are more than fifty times brighter than commercial GaP LEDs which produce outputs peaked in the yellow-green at 555 nm. Although the presence of Te broadens the emission somewhat (FWHM = 245 meV) since Te acts as an isoelectronic hole trap, most of the light from the ZnTeSe device occurs in the blue-green to green spectral regions from 500-550 nm. The LED emission appears as a vibrant deep-green to the human eye.

Table I summarizes the results. Measured light outputs at 10 mA are given for each of the three types of devices tested. External quantum efficiencies $\eta_{q_{\text{ext}}}$, external power efficiencies $\eta_{p_{\text{ext}}}$, and luminous efficiencies $\eta_{v_{\text{ext}}}$ obtained using Eqs. (1), (2) and (3), are also listed in the table. In addition, the internal quantum efficiency $\eta_{q_{\text{int}}}$ of each of the devices was estimated using the expression [5]:

$$\eta_{q_{\text{int}}} = \frac{\eta_{q_{\text{ext}}}}{\eta_{\text{opt}}} \quad \text{(photons/electron)}$$  (4)
### TABLE I. Summary of blue/green LED characteristics.

<table>
<thead>
<tr>
<th>LED Type</th>
<th>Peak Wavelength (nm)</th>
<th>Output Power (10 mA) (mW)</th>
<th>$\eta_{q_{ext}}$ (photons/electron)</th>
<th>$\eta_{q_{int}}$ (photons/electron)</th>
<th>$\eta_{p_{ext}}$</th>
<th>$\eta_{v_{ext}}$ (lumens/watt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCdSe</td>
<td>489</td>
<td>0.327</td>
<td>1.3%</td>
<td>7%</td>
<td>1.0%</td>
<td>1.6</td>
</tr>
<tr>
<td>InGaN [17]</td>
<td>450</td>
<td>1.04</td>
<td>3.8%</td>
<td>15%</td>
<td>3.0%</td>
<td>3.6</td>
</tr>
<tr>
<td>ZnTeSe</td>
<td>512</td>
<td>1.30</td>
<td>5.3%</td>
<td>28%</td>
<td>4.0%</td>
<td>17.0</td>
</tr>
</tbody>
</table>
TABLE II. Comparison of various visible light-emitting diodes.

<table>
<thead>
<tr>
<th>LED Type</th>
<th>Peak Wavelength</th>
<th>Device Structure</th>
<th>Ext. Quantum Efficiency %</th>
<th>Performance lumens/watt</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAsP</td>
<td>700 nm</td>
<td>HJ</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>650 nm</td>
<td>DH-TS</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>AlInGaP</td>
<td>620 nm</td>
<td>DH</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>AlInGaP</td>
<td>585 nm</td>
<td>DH</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>AlInGaP</td>
<td>570 nm</td>
<td>DH</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>GaP</td>
<td>555 nm</td>
<td>HJ</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>ZnTeSe</td>
<td>512 nm</td>
<td>DH</td>
<td>5.3</td>
<td>18</td>
</tr>
<tr>
<td>ZnCdSe</td>
<td>489 nm</td>
<td>DH</td>
<td>1.3</td>
<td>1.7</td>
</tr>
<tr>
<td>SiC</td>
<td>470 nm</td>
<td>HJ</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>InGaN</td>
<td>450 nm</td>
<td>DH</td>
<td>3.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>
where $\eta_{\text{opt}}$ is the optical efficiency of the LED lamp which can be estimated using standard equations [15]. In these calculations, refractive indices of $n_{\text{epoxy}} = 1.50$, $n_{\text{ZnSe}} = 2.826$ at 489-512 nm, and $n_{\text{GaN}} = 2.480$ at 450 nm were used. For II-VI blue/green LEDs grown on a transparent ZnSe substrate, we obtained $\eta_{\text{opt}} \sim 0.186$. By way of comparison, if an absorbing substrate such as GaAs is used, $\eta_{\text{opt}}$ is only $\sim 0.037$, which significantly limits the maximum external efficiency of the device. For the InGaN LED, which was grown on sapphire, $\eta_{\text{opt}} \sim 0.251$. Thus, as calculated from Eqs. (4) and listed in table I, the ZnCdSe blue LED operates with internal quantum efficiency $\eta_{\text{qint}} \sim 7\%$ while the Nichia InGaN blue LED exhibits $\eta_{\text{qint}} \sim 15\%$ at 300K. The light output from both of these devices may be expected to increase significantly as future improvements in epitaxial growth techniques increases $\eta_{\text{qint}}$. For the ZnTeSe green LED, $\eta_{\text{qint}} \sim 28\%$. This is comparable to the internal efficiencies of commercial super-bright red LEDs and gives direct evidence that the Te isoelectronic sites in ZnTeSe provide an excellent mechanism for very efficient green light emission at room temperature. Table 2 compares characteristics of various visible LEDs.

The key issue concerning the development of II-VI blue/green light emitters which remains to be addressed is that of device degradation. All of the II-VI laser diodes and LEDs produced to date suffer from degradation of their light output [18,19]. In the case of laser diodes, the longest published cw lifetime at room temperature is only nine minutes [20]. A homoepitaxial growth approach using ZnSe substrates rather than GaAs has resulted in improved lifetimes for LEDs produced at NCSU. Fig. 3 shows 300K degradation data for two ZnTeSe LEDs operated continuously at two different dc current densities. The observed decrease in optical output power $\Phi$ obeys the equation

$$\Phi = \Phi_0 \exp [-t/\tau],$$

(5)
$\Phi = \Phi_0 \exp \left[ -\frac{t}{\tau} \right]$ 

Figure 3. Natural log of $\Phi/\Phi_0$ versus time for ZnSe/ZnTeSe green LED.
where $\tau$ is the exponential lifetime of the device. For a current density $J = 15$ A/cm$^2$, $\tau = 675$ hrs. For a higher current density $J = 50$ A/cm$^2$, the LED lifetime $\tau = 350$ hrs. Thus, the degradation process accelerates as the current density flowing through the device increases. Preliminary x-ray diffraction and transmission electron microscopy experiments indicate that the dislocation density in present devices grown on ZnSe is about $10^6$/cm$^2$. Improvements in nucleation and growth to reduce dislocation densities are expected to increase the device lifetime substantially in the months ahead. We estimate the dislocation densities of $10^4$/cm$^2$ or less will be needed in order to insure long device lifetimes. We believe that this level of structural perfection is achievable.

In summary, we have demonstrated world-class blue and green LEDs based on II-VI heterostructures grown on ZnSe substrates. The blue LEDs produce 327 $\mu$W (10 mA, 3.2 V), with the light output sharply peaked at 489 nm, and exhibit an external quantum efficiency $\eta_{\text{ext}} = 1.3\%$. The green LEDs produce 1.3 mW (10 mA, 3.2 V) peaked at 512 nm, corresponding to an external quantum efficiency $\eta_{\text{ext}} = 5.3\%$. In terms of photometric units, the luminous performance $\eta_{\text{vext}}$ of the devices is 1.6 lumens/watt (blue) and 17 lumens/watt (green), respectively, when operated at 10 mA. The devices also show improved lifetimes compared with similar structures grown on GaAs, although additional improvements are needed before commercialization of ZnSe-based devices becomes a reality.

**STUDENT INVOLVEMENT:**

Two Ph.D. students were trained under the above program of research. Jack Ren received his degree in 1994 and is currently employed by Cree Research, Inc. David Eason received his degree in 1994 and is currently employed by Eagle Picher Laboratories in Miami, OK.
PUBLICATIONS: The following presentations and papers resulted from work completed under the above program:


INVITED PRESENTATIONS:


11. "Blue/Green Lasers and LEDs Based on II-VI Heterostructures", Chiba University, Japan (1993).


13. "MBE Growth and Properties of II-VI Light Emitting Structures", Hong Kong University of Science and Technology, Hong Kong, China (1993).


17. "High-Brightness Blue and Green LEDs on ZnSe", Eagle-Picher Research Laboratory, Miami, OK (1994).

