Growth of Thin Film for Waveguide Laser: "Development of Chromium Doped Zn Chalcogenides as Efficient, Widely Tunable Mid-Infrared Lasers"

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Principal Investigators: Arnold Burger (Fisk University) and Stephen A. Payne (LLNL)  
Fisk Collaborators: Kuo-Tong Chen, and Henry Chen
LLNL Collaborators: K. Schaffers, and R. H. Page
Students: Troy D. Joumigan, Ms. Devona Beard and Ms. Jacqueline J. Robinson

Abstract
The incorporation of chromium in wide bandgap semiconductors is becoming a topic of interest in the development of efficient and compact tunable (range of 2 - 3 μm) solid state mid-infrared lasers operating at room temperature. In the search for optimized procedures of doping that will raise the chromium concentration to a level of 10¹⁸ ions/cm³, we have developed a diffusion process in the temperature range of 750 - 950 °C. However, optimization needs to be made during this process to preserve the optical transparency of the doped samples. The experimental data will be discussed in terms of dopant diffusivity, distribution of defects and crystal homogeneity.

Objectives
This project was initiated under the LLNL Research Collaborations Program (RCP) in FY94. As initially defined, the project aimed at developing a compact, diode pumped solid-state mid-infrared tunable laser based on Cr²⁺ doped zinc chalcogenides (ZnSe, ZnS), as recently discovered at LLNL. As preliminary results showed promising gain cross sections, low non-radiative decay losses and long emission lifetimes at room temperature, scientific challenges remained in the area of optimization of dopant concentrations and optical passive losses in the crystals. Graduate students participation and training is considered an integral part of this investigation. It is expected that the program will increase the involvement of minority science students, and motivate them to pursue careers in the area of photonics. General applications such as environmental (remote sensing and pollution monitoring) and medical ("optical scalpel") applications of such a laser can be envisioned. There is also a growing need for compact light sources required in Laser Infrared Detection and Ranging (LIDAR).

Progress
Tetrahedrally-coordinated Cr²⁺ ions were reported to be especially attractive as lasants on account of high luminescence quantum yields for emission in the 2000 - 3000 nm range. Radiative lifetimes and emission cross sections of the upper E state are respectively 10 μsec and 10⁻¹⁸ cm². (R. H. Page et al, Ref. 6). Particularly attractive is the possibility of laser-diode pumping of the Cr²⁺ systems (the associated absorption band peaks at ~1800 nm).
In this project a new diffusion doping process has been developed for incorporation of Cr²⁺ ion into ZnSe wafers. This process has been successfully performed under isothermal conditions, at
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temperatures above 800 C. Concentrations in excess of $10^{19}$ Cr$^{2+}$ ions/cm$^3$, an order of magnitude larger than previously reported in melt grown ZnSe material, have been obtained by diffusion doping, as estimated from optical absorption measurements. By assuming the equilibrium diffusion depth as 0.1 cm, which is deeper than the requirement to be used as solid state laser material, the diffusivity, $D$, can be estimated by a thin film diffusion model [10]. In this model, the equilibrium diffusion depth, $x$, is defined as $x = 2(Dt)^{1/2}$, where $t$ is the diffusion time. By applying 0.1 cm for $x$ and 5 days annealing time, the diffusivity was estimated to be in the $10^4$ cm$^2$/sec which lower than Ag ($10^7$) and Cu ($10^6$). Figure 4 show the AFM images on freshly cleaved Cr$^{2+}$ doped ZnSe for 2 days at 950°C.

As shown in Table 1, solubility limit of Cr$^{2+}$ in ZnSe has not been reached under current experimental conditions, and the Cr$^{2+}$ concentration should continue to increase as function of annealing time and temperature. We did not observe significant effects in Cr$^{2+}$ concentration and lifetime (under the same diffusion conditions) that could be related to the crystallinity (single or poly-crystal) of ZnSe.

### Table 1. Summary of diffusion doping parameter, resulting Cr$^{2+}$ concentration, resistivity and lifetime.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Temperature (°C)</th>
<th>Annealing Time (days)</th>
<th>Concentration Cr$^{2+}$ (cm$^3$)$\times10^{16}$</th>
<th>Lifetime (usec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#12413: Bridg. Poly.</td>
<td>800</td>
<td>2</td>
<td>0.05</td>
<td>6</td>
</tr>
<tr>
<td>#12413A: Bridg. Poly.</td>
<td>850</td>
<td>5</td>
<td>0.24</td>
<td>5</td>
</tr>
<tr>
<td>#12429: Bridg. Twinned-top</td>
<td>900</td>
<td>5</td>
<td>0.19</td>
<td>5</td>
</tr>
<tr>
<td>#12429A: Bridg Twinned-bot.</td>
<td>900</td>
<td>5</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>#12428: Bridg. Poly.</td>
<td>900</td>
<td>5</td>
<td>0.18</td>
<td>3</td>
</tr>
<tr>
<td>#12427: Bridg. Poly-top</td>
<td>950</td>
<td>2</td>
<td>0.38</td>
<td>2.5</td>
</tr>
<tr>
<td>#12426: Bridg. Poly-bot.</td>
<td>950</td>
<td>2</td>
<td>0.33</td>
<td>3.1</td>
</tr>
<tr>
<td>#12430: SPVT, Single</td>
<td>950</td>
<td>2</td>
<td>0.17</td>
<td>6</td>
</tr>
<tr>
<td>SPVT, Single</td>
<td>1000</td>
<td>5.5</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

The presentation and publication of results is strongly encouraged and considered an integral part of graduate training. The department has also developed scientific cooperation with a number of national research labs and there is the opportunity for participation by our students in summer training programs which are helpful in acquiring additional expertise for pursuing careers in research. Two undergraduates (Ms. Devona Beard and Ms. Jacqueline J. Robinson) and one graduate student (Mr. Troy D. Journigan), as well as two summer interns participating in the 1996 summer research program for undergraduates, have participated in the project and the results were communicated at national meetings [1-6].
References


