

## Eagle-Picher Research Laboratory

**Brighter, Longer Lasting Blue and Green Lasers and LEDs**

*In the early 1990s, true green or blue light-emitting diodes (LEDs) with enough intensity for commercial applications were not available. Eagle-Picher and North Carolina State University (NCSU) had achieved groundbreaking developments in creating zinc selenide blue and green lasers and LEDs, but needed financial assistance to continue the research and development. With funding from the Advanced Technology Program (ATP), Eagle-Picher and NCSU (a subcontractor) partnered to develop blue LEDs that were approximately 40 times brighter than those commercially available and green LEDs that were 50 times brighter than those commercially available. Near the end of the project, however, a Japanese company released a blue LED with a longer life span. In response, Eagle-Picher redirected its research into zinc oxide-based lasers and LEDs.*

**COMPOSITE PERFORMANCE SCORE**

(based on a four star rating)

**No Stars**

Research and data for Status Report 92-01-0109 were collected during October - December 2001.

**Short-Wavelength Lasers Impeded by Crystal Degradation**

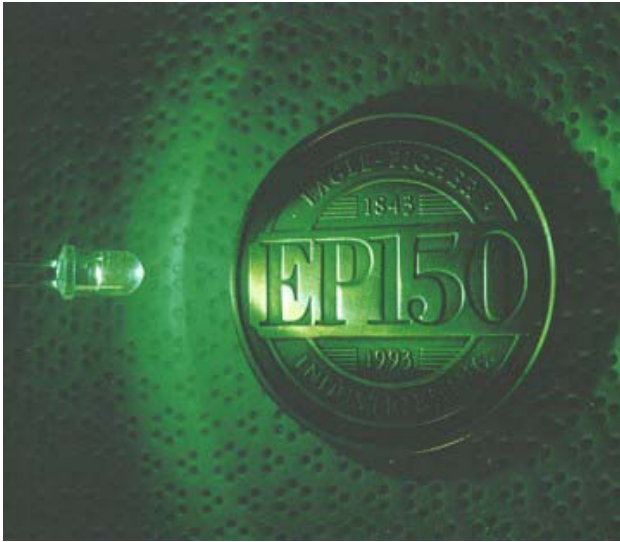
In the early 1990s, the laser industry was using zinc selenide (ZnSe) and gallium arsenide (GaAs) to produce various types of lasers. These two compounds have different thermal coefficients of expansion, however, and they expand and contract at different rates and by different amounts. Consequently, when ZnSe and GaAs are joined together, the bonds between them fail and degradation problems are frequently encountered, resulting in substantial limitations of the capabilities of various laser products.

Furthermore, when this ATP project began in 1993, no one in the industry had been able to develop true green or blue light-emitting diodes (LEDs) that lasted more than a few seconds before the crystal structures became riddled with light-quenching defects. In addition, LEDs marketed as "green" lacked intensity and were actually a disappointing hue of yellow green.

Eagle-Picher Research Laboratory and North Carolina State University (NCSU) had achieved groundbreaking developments in this field of research. Their funding was limited, however, so additional financing was required in order to continue with the research and development of this breakthrough technology. Consequently, they approached ATP for financial assistance to jump-start the development of commercially viable ZnSe blue and green lasers as well as LEDs.

**Multiple Industries Expected to Benefit from New Technology**

The proposed technology was expected to benefit multiple industries and end users. The shorter wavelength blue/green lasers resulting from this technology could store more information than the red lasers that were at the heart of optical communications. Moreover, the shorter wavelengths could lead to data recording and storage systems with much greater capacities than offered by the lasers in use at the time.



Eagle Picher's green LEDs were 50 times brighter than existing GaP green LEDs.

It was anticipated that the following markets would be affected by this technology:

- Flat panel displays
- Automotive displays
- Information storage
- Color printing
- Optical communications
- Medical lasers
- Optical computing

### Partnership Overcomes Obstacles

The goal of this ATP project was to develop high-efficiency, long-lifetime blue/green lasers and LEDs using homoepitaxy of ZnSe-based structures on ZnSe substrates. (Homoepitaxy refers to the growth of a crystalline substance (ZnSe) on a crystalline substrate of the same material.) To achieve this goal, the project objectives included development of substrate and device fabrication. Eagle-Picher planned to complete the substrate development; NCSU, under subcontract, would focus on device fabrication.

Eagle-Picher believed that its patented seeded physical vapor transport (SPVT) bulk crystal growth method provided a solid base for this project because it was capable of growing ZnSe crystals large enough for commercial purposes, whereas other methods were incapable of growing these larger crystals.

Growing crystals was just one step in the complex development cycle. The next step, which plagued developers for some time, involved depositing ZnSe layers onto GaAs layers. This process was difficult because the respective spacing between the atoms of the two layers did not match, which led to weaknesses within the crystal substructures. Fortunately, NCSU's molecular beam epitaxy (MBE) process addressed this issue by allowing the building and varying of crystal structures, atomic layer by atomic layer.

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At the start of this project, only semi-insulating ZnSe substrates were available, so the device structures were designed to utilize them. However, conductive substrates were essential to the successful development of efficient short-wavelength blue and green lasers, as well as diodes. As conductive substrates became available, the developers created device structures to use those substrates as the back contact.

### Researching the Parameters of Bulk Crystal Growth

Initially, four furnaces were used to grow crystals for this project. One of these furnaces supplied state-of-the-art substrates to NCSU. The remaining three furnaces were used in studies to improve the growth conditions. Through a series of designed experiments, researchers investigated growth temperature, seed type, seed preparation, growth pressure, cooling conditions, and growth rate. As improvements were identified, they were incorporated into the procedures for the production furnace. Initial efforts at NCSU were directed at MBE growth of ZnSe and related alloys on

three different orientations of ZnSe substrates. All substrates supplied to NCSU were fully characterized by Eagle-Picher.

### **SPVT Method Proves Successful in Bulk Crystal Growth**

By the end of the ATP project in 1996, the yield, size, and crystalline quality of the ZnSe crystals grown by the SPVT method had notably improved. Yields approaching 100 percent were achieved in production-scale runs. Three-inch-diameter crystals with quality similar to two-inch-diameter crystals were produced. Moreover, growth of conductive crystals for injection laser fabrication was remarkably successful. Net carrier concentrations as high as  $2 \times 10^{18}/\text{cm}^3$  were achieved, with mobilities similar to those of MBE films of the same net carrier concentration. These significant milestones aided in the development of short-wavelength blue and green lasers.

In addition to production improvements in the SPVT method, developers made significant strides in understanding the ZnSe SPVT crystal growth process. At the onset of the project, control of the ZnSe SPVT process was good, but the parameters used for crystal growth were empirically determined. To develop a true production-scale manufacturing facility that was capable of producing extremely high yields at a low cost, it was essential to understand the actual control mechanisms for the SPVT method. By the conclusion of this project, models of the control mechanisms permitted the determination of optimum operating parameters based on desired product specifications. The models also could identify equipment problems at an early stage to avoid the expense of making long crystal growth runs with poor yields. Without these models, it was necessary to wait as long as two weeks to determine the yield of the crystal growth runs.

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Although these accomplishments were impressive, Eagle-Picher believed that the most significant result of

the crystal growth optimization study was the dramatic improvement in the crystalline quality of the undoped, semi-insulating ZnSe being grown. Multiple test results verified that the world's best crystalline quality, large-area ZnSe wafers were being routinely produced.

Another first achieved during this project was the doping (that is, the introduction of an element that alters the conductivity) of the bulk crystals to achieve n-type, or positive, conductivity. This doping was necessary for the production of short-wavelength blue and green lasers. In fact, as the level of doping is increased, so is the intensity of the light emitted by lasers and LEDs. According to Eagle-Picher, at the conclusion of the project it had achieved the highest n-type doping concentration ever obtained in large-area ZnSe crystals with high crystalline quality. This achievement enabled the production of the first practical, short-wavelength injection lasers.

### **Prototype LEDs Are Brighter than Existing Commercial LEDs**

The project's second objective, the device fabrication, also met with technical success. NCSU was able to develop functional blue and green LEDs from the improved wafers created at Eagle-Picher. The blue LEDs were approximately 40 times brighter than commercial silicon carbide (SiC) LEDs, and the green LEDs were 50 times brighter than gallium phosphide (GaP) green LEDs. In addition to being brighter, the light emitted by these LEDs was purer than that available from the commercial blue and green LEDs available at the time.

Although the development of the lasers using homoepitaxy of ZnSe on ZnSe substrates was slower than expected, the first homoepitaxial ZnSe injection laser was accomplished before the end of the project. At the time, the laser operated in pulse mode only.

### **Prototypes Fail to Achieve Life-Span Objectives**

With the development of prototypes that incorporated the new technology, scale-up and commercialization were almost within sight. Unfortunately, as the project neared its conclusion, a Japanese firm, Nichia, successfully completed the development of gallium nitride (GaN) blue LEDs that took the industry by storm.

Nichia's LEDs and lasers were more appealing because their operating life spans exceeded 10,000 hours, whereas the prototypes that Eagle-Picher and NCSU had developed were only capable of operating up to 8,000 hours. This difference in laser and LED operating life spans prompted Eagle-Picher to abandon its original plan of developing and commercializing ZnSe-based blue and green lasers and LEDs.

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## **Conclusion**

After the conclusion of the ATP project, Eagle-Picher used the knowledge it had gained from the project to focus its efforts on developing zinc oxide (ZnO)-based lasers and LEDs. ZnO has the potential to produce lasers and LEDs that are stronger than those based on ZnSe.

## PROJECT HIGHLIGHTS

### Eagle-Picher Research Laboratory

**Project Title:** Brighter, Longer Lasting Blue and Green Lasers and LEDs (Development of Blue/Green Emitters Using Homoepitaxial Zinc Selenide (ZnSe)-Based Heterostructures)

**Project:** To apply newly developed production technologies to the fabrication of high-efficiency, long-lived blue/green lasers and LEDs.

**Duration:** 3/1/1993-2/28/1996

**ATP Number:** 92-01-0109

#### Funding (in thousands):

ATP Final Cost	\$ 1,759	59%
Participant Final Cost	<u>1,200</u>	41%
Total	\$ 2,959	

**Accomplishments:** Eagle-Picher was unable to achieve its goal of LED life spans of 10,000 hours; instead the life spans reached approximately 5,000 to 8,000 hours. However, the project achieved successes in substrate development, laser and LED output power, and substrate quality. Eagle-Picher and NCSU developed blue and green prototype lasers and LEDs that exhibited superior output capabilities. The blue LEDs were approximately 40 times brighter than commercial SiC LEDs, and the green LEDs were 50 times brighter than GaP green LEDs. In addition to being brighter, the light emitted by these LEDs was purer than the light from the commercially available blue and green LEDs. Eagle-Picher developed three-inch-diameter crystals with superior quality characteristics. At the conclusion of the project, the company had developed crystals capable of achieving n-type conductivity. This achievement was the highest n-type doping concentration ever obtained in large-area ZnSe crystals with high crystalline quality.

**Commercialization Status:** Eagle-Picher's laser and LED prototypes had life spans of approximately 5,000 to 8,000 hours; however, Nichia, a Japanese firm, successfully developed a GaN blue LED with a life span in excess of 10,000 hours. Because of its inability to meet the 10,000-hour product life-span, Eagle-Picher suspended further research and development of ZnSe-based lasers and LEDs in order to pursue other alternatives.

**Outlook:** Because of difficulties associated with the life spans of ZnSe-based lasers and LEDs and competition from abroad, the outlook for this technology is poor. Eagle-Picher has redirected its focus to ZnO-based lasers and LEDs.

**Composite Performance Score:** No stars

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#### Subcontractors:

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