ULTRAWIDE BANDGAP Materials in the Spotlight

Lawrence Livermore researchers explore controlling semiconductors with light, rather than chemical impurities, to optimize for high-power and laser applications.

THE semiconductor materials at the heart of most electronic devices have shaped computing, power distribution, optical, and communication technologies. As demands for improved performance evolve, so must semiconductor materials evolve to support high-power applications. For example, silicon cannot efficiently control the voltage levels handled by switches that integrate alternative energy sources into the nation's electric grid. Electric vehicles demand materials that can bear high electric fields for improved charging efficiency.

Semiconductor materials such as silicon carbide and gallium nitride—wide bandgap (WBG) semiconductor materials—operate at higher temperatures, voltages, and frequencies, enabling smaller and more efficient components for lower cost, high-power applications. The bandgap of a semiconductor is the energy required for an electron to move from a lower energy state (the valence band) to a higher energy, free state (the conduction band). In making this jump, the electron leaves behind an empty space (hole) in the valence band that enables electron movement in that band as well.

The wider the bandgap, the higher the energy. Therefore, ultrawide bandgap (UWBG) semiconductor materials tolerate even higher voltages with lower power losses than WBG materials. UWBG materials promise to improve high-power devices for grid control along with laser applications and technologies such as diode-based additive manufacturing, in which an optically addressable light valve (OALV) shapes high-power laser light in programmed, layer-by-layer images to build parts.

The Right Time with the Right Tools

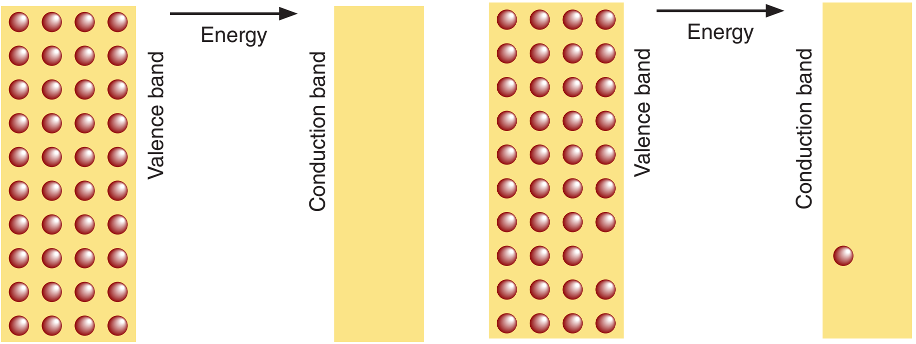
Understanding the growing need for high-power technology, Department of Energy (DOE) energy frontier research centers (EFRCs) have turned their attention to UWBG materials. The topic is not new to Livermore materials engineer Lars Voss. "High-power semiconductor research is a niche at Lawrence Livermore compared to other national laboratories," he says. "The Laboratory builds devices in different ways to meet different requirements than basic science centers. We've long realized the need to move beyond the last decade's state of the art."

No single UWBG material stands out as the best candidate for high-power devices. Diamond offers superior electron mobility and thermal conductivity but does not offer the large-area substrates required for additive manufacturing. Gallium oxide possesses the availability of low-defect, large substrates but represents a compromise in electron transport and thermal properties compared to diamond. Aluminum nitride registers closer to diamond's energy and thermal characteristics but at a higher cost and lower substrate area than gallium oxide.

Dopants—impurities introduced to a semiconductor crystal—alter the number of charge carriers (electrons and holes) to tailor a semiconductor's electrical properties. However, UWBG materials cannot be doped with impurities that are able to achieve the broad conductivity control required for high-power applications.

An alternative approach to shape the properties of semiconductor materials is to use photons, rather than impurities, to generate electron carriers and control the conductivity of these materials, an approach Lawrence Livermore has used with great success in laser and other mission-focused programs. Photogenerated carriers are excited directly across the bandgap from the valence band to the conduction band, the way photons are converted to electrical current in solar cells. However, to generate free carriers, an exceptionally wide bandgap requires high-energy photons such as those from deep, ultraviolet (UV) light sources, which is an impractical requirement for deployable systems.

To overcome the challenge of controlling the UWBG materials' electrical properties, a team of Lawrence Livermore researchers led by Voss proposed to introduce un-ionized dopants, with energy levels deep within the materials' bandgap, that can be excited with lower energy light, generating free carriers. "Other institutions are focused on electronic approaches to build UWBG devices," says Voss. "However, they find themselves unable to achieve broad conductivity. Sub-bandgap, optical excitation provides a universal, material-agnostic approach to building devices to meet high-power needs. Livermore is the perfect place to do this because we have applied the same approach using other material systems for more than a decade."



The bandgap of a semiconductor is the energy required for an electron to move from a lower energy state (the valence band, on the left side in each image) to a higher energy, free state (the conduction band). In making this jump, as indicated in the image on the right, the electron leaves behind an empty space (hole) in the valence band that enables electron movement in that band as well.

Earlier Laboratory Directed Research and Development (LDRD) projects at Lawrence Livermore provided a foundation for a new proposal. Projects exploring silicon carbide and diamond photoconductive switches led to improved defect absorption of the materials and increased photo response, exciting higher current as voltages increased. Livermore research teams had also demonstrated significantly (100x) higher electrical fields across increasingly thinner switches. Voss and materials scientist Vincenzo Lordi saw an opportunity to expand on past LDRD projects by applying precise computational approaches to predict the electronic qualities of ideal dopants in UWBG materials and how the dopants would react to light. "We recognized that a new project could build quantitatively on earlier Livermore projects, which had only crudely predicted many of these properties," says Lordi. "With the more powerful supercomputers now at Livermore, we can advance the calculations to direct experimental doping efforts."

In 2021, Voss, Lordi, and a Livermore team of chemical, electrical, materials, and mechanical engineers embarked on a new LDRD project to generate mobile charge carriers in UWBG materials with sub-bandgap photons, synthesize optimal UWBG materials, and demonstrate devices using optimized materials. "This project came at the opportune time from a technology and a need standpoint to dive into these materials and solve the problems Livermore cares about," says Voss. "The LDRD project combines materials discovery with a demonstration of real devices that can ultimately be scaled to move up the technical readiness scale,” says Voss.

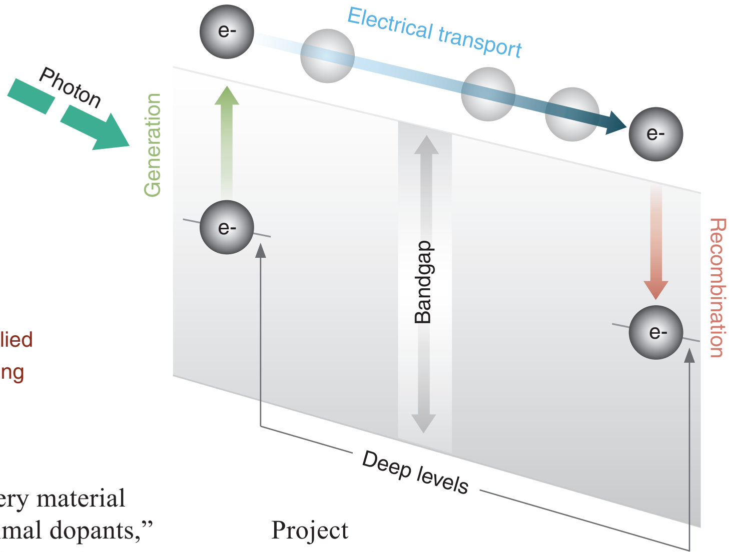
The research can enhance the Laboratory’s opportunities to support DOE’s Office of Energy Efficiency and Renewable Energy and the Advanced Research Projects Agency–Energy (ARPA–E) as well as future EFRC calls in the power electronics fields. Looking beyond the DOE enterprise, Lordi observes, “Power switching on the order of 10 times more efficient can lower energy use at data centers, which are a major consumer of energy and, hence, a notable contributor to greenhouse gas emissions. A pathway to radiation-tolerant electronics for use in extreme space environments may be another area of impact.”

Closer to home, the researchers saw an opportunity to apply their findings to fabricating OALVs with optimized materials to better withstand the high fluence of laser operations at the National Ignition Facility (NIF) and other advanced laser facilities. (See sidebar, “More Shots, More Potential for Success.”)

Iterative Innovation

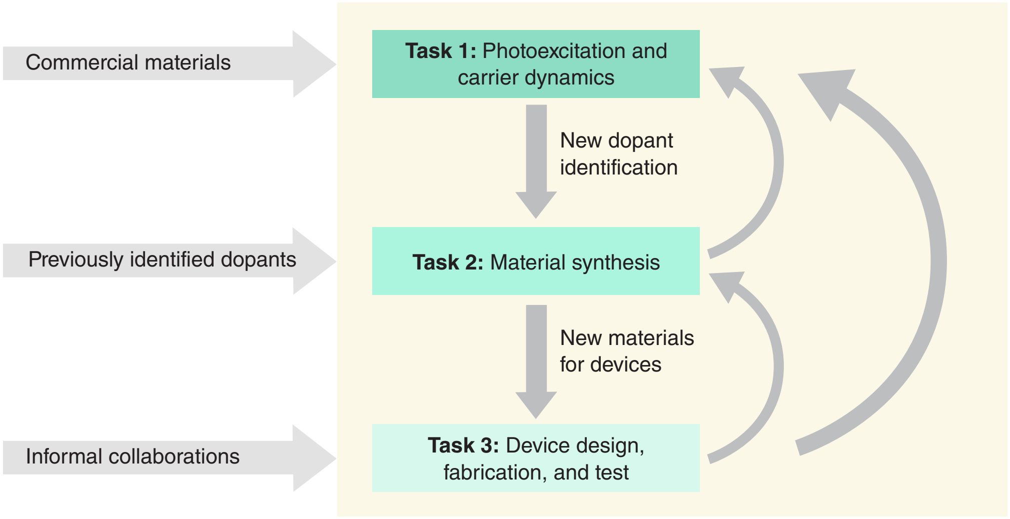
The LDRD project proposed three research tasks to be carried out simultaneously. In this way, each task would inform and refine the project overall, improving material candidates along the way to spur innovation more quickly.

In the first task, a group led by Livermore scientist Joel Varley investigated material choices and candidate dopant atoms to more favorably tune absorption and photoconductive response. Varley’s group performed predictive materials simulations using hybrid-functional density functional theory, which uses details of a material’s electronic structure to consider how it would respond to optically generated carriers, targeting the favorable combination of strong absorption and higher conductivity. “Every material has a potential set of optimal dopants,” says Varley. “The desired optical response in an OALV is largely dictated by fundamental properties of the photoconductive material as well as impurities or suitable defects that lead to photo absorption and generate the conductivity. Increasing computing automation enabled us to explore appropriate dopants more accurately and in less time than with earlier computing capabilities, and many years faster than trial and error.”



The properties of ultrawide bandgap (UWBG) materials can be enhanced by photoexcitation rather than doping—adding impurities to a semiconductor material. In photoexcitation, sub-bandgap light excites an electron from the deep, ultraviolet level, and the electron moves under an applied electric field before recombining back into the deep level.

Project partners at the University of California at Santa Barbara (UCSB), Washington State University (WSU), and Vilnius University provided valuable insight and materials research data to Varley and his team. “When adding new dopant sources to the system, we consider theoretical findings and factors such as material purity, vapor pressure, and literature regarding whether the material will linger in the system after growth,” says UCSB researcher Steve Rebollo.



An iterative project plan enabled findings from each task to inform and improve outcomes over the three-year duration of the project rather than constrain research in later tasks to a limited number of dopant and material candidates.

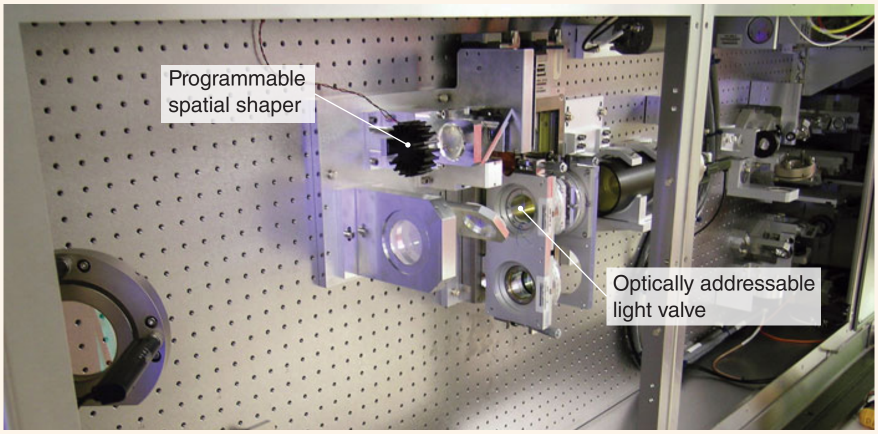
More Shots, More Potential for Success

Lawrence Livermore's National Ignition Facility (NIF) stands to gain from the Laboratory Directed Research and Development (LDRD) project to explore ultrawide bandgap (UWBG) photoconductive devices. NIF, the world's highest-energy laser system simulates extreme temperature and pressure conditions to advance understanding of fusion ignition and thermonuclear burn, relevant to stockpile stewardship. Programmable spatial shapers (PSSs) at NIF modulate laser intensity in the optical beam path to address laser-induced damage on optical components, which increases shots per year by reducing maintenance time and costs. Optically addressable light valves (OALVs) with wide bandgap bismuth silicon oxide (BSO) as a photoconductive layer enable drop-in retrofit of NIF's PSS system.

"The PSS is a critical component for preventing degradation of downstream optical elements under laser illumination," explains engineer Sara Harrison, a member of the LDRD project team. "The practice is to block light from shining in areas where flaws exist in the optics. While this protects the optics, light is thrown away unnecessarily with the present configuration. Therefore, NIF is eager to improve PSS specifications by exploring materials that enable the position of the OALVs to be shifted in the beam lines."

Livermore scientist and LDRD project team member Joel Varley adds, "The current BSO device can only withstand so much laser fluence, and the technology cannot be scaled to a larger size to achieve the clear aperture areas required. Using more robust materials in light valves enables more energy per shot." A new design incorporating an ultrawide bandgap (UWBG) photoconductor would enable higher power operation. A new OALV design will rely on photoconductive semiconductors that can be grown in large boules, heavily doped to form contact layers, and capable of withstanding fluences of 1 to 2 Joules/square centimeter area for adoption in high-power laser systems.

"The connection to NIF makes the UWBG materials research even more exciting," says project advisor Vincenzo Lordi. "Applying the LDRD project's findings at NIF will be impactful and improve performance dramatically."



The programmable spatial shapers package incorporates optically addressible light valves to extend the operational lifetime of the National Ignition Facility's high-energy laser optics by obscuring laser light where flaws exist in optical components, limiting further damage during subsequent shots.

"Following growth, we analyze a dopant's effect on material growth using atomic force microscopy, x-ray diffraction, and other techniques to probe the surface morphology and crystalline quality, respectively. We shared this information with the Livermore team."

The UCSB researchers have found gallium oxide films attractive due to the high purity of the epitaxial material and its ability to withstand high-power laser pulses. "Gallium oxide's qualities translate into experimental demonstrations of the highest laser-induced damage threshold (LiDT) among UWBG semiconductors," says UCSB's Sriram Krishnamoorthy.

Researchers from WSU's Institute of Materials Research discussed possible dopants that might have the desired optoelectronic properties with the Livermore team and gained valuable information in the exchange. "Working with Livermore enabled us to see the higher-level device side and participate in designing crystals to meet the end needs of those devices," says WSU scientist John McCloy. His colleague Matt McCluskey adds, "To test the robustness of materials proposed for an OALV, candidate materials such as gallium oxide, aluminum nitride, and diamond are irradiated with intense laser pulses and then characterized using optical techniques. WSU uses a deep-UV photoluminescence system to investigate defects in UWBG semiconductors with a high level of detail. From the results of these fundamental studies, we aimed to develop a way to screen good versus bad crystals."

To date, Varley's team has computationally screened thousands of materials, investigating their intrinsic ability to generate a stronger response to photoexcitation. "Our results point to tailored materials with properties matched to end-use applications," says Varley. A number of materials offer the promise of high photo response, provided that suitable dopants and defects can be introduced and lead to absorption at the desired energies. To that end, the team has leveraged atomistic-level simulations to continue refining dopant candidates that tune to optical response.

Taking the next step, the team, in concert with academic partners, synthesized materials with target dopants identified from theory to yield energy levels suitable for desired visible light excitation. WSU has synthesized single crystals while UCSB grew epilayers (thin films) onto crystals. These materials have been characterized and processed into OALVs, with promising optical responsivity. “We have focused on a beta composition of gallium oxide, a UWBG semiconductor commercially available in large-area substrates ideal for fabricating large-format OALVs,” says Varley.

Synthesis Success

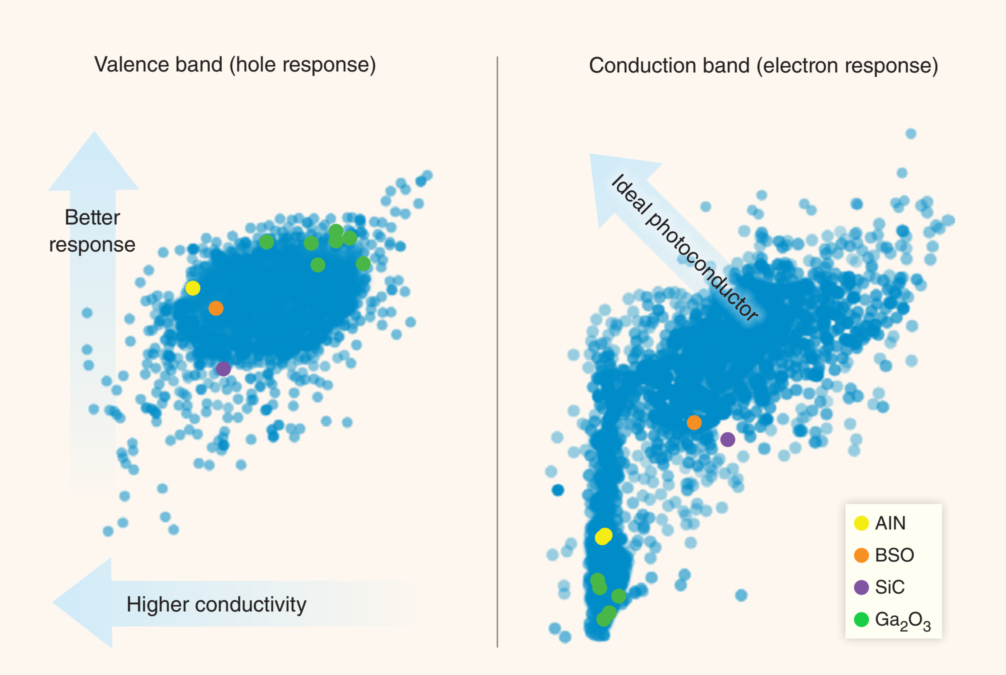
The second project task focused on procuring and synthesizing material candidates to identify materials with ideal properties such as carrier generation, recombination, and transport for high-power devices. The task team, led by engineer Clint Frye and former Livermore scientist Andrew Lange, started with the top contender: gallium oxide. Gallium oxide offers the advantage of providing large substrates. Other candidate materials—diamond crystals and aluminum nitride—were also grown or procured and then characterized and tested for photoconductive properties during this task.

Continuing the project’s iterative research format, the team worked with commercial vendors to source UWBG materials while candidate materials continued to undergo growth and custom doping for optimized outcomes. WSU’s unique capability for growing gallium oxide crystals combined with data informing custom dopants enabled the growth of bulk beta gallium oxide crystals. With repeated characterization and further computational modeling, the team learned process improvements to incorporate the dopant and activate desired material qualities such as conductivity.

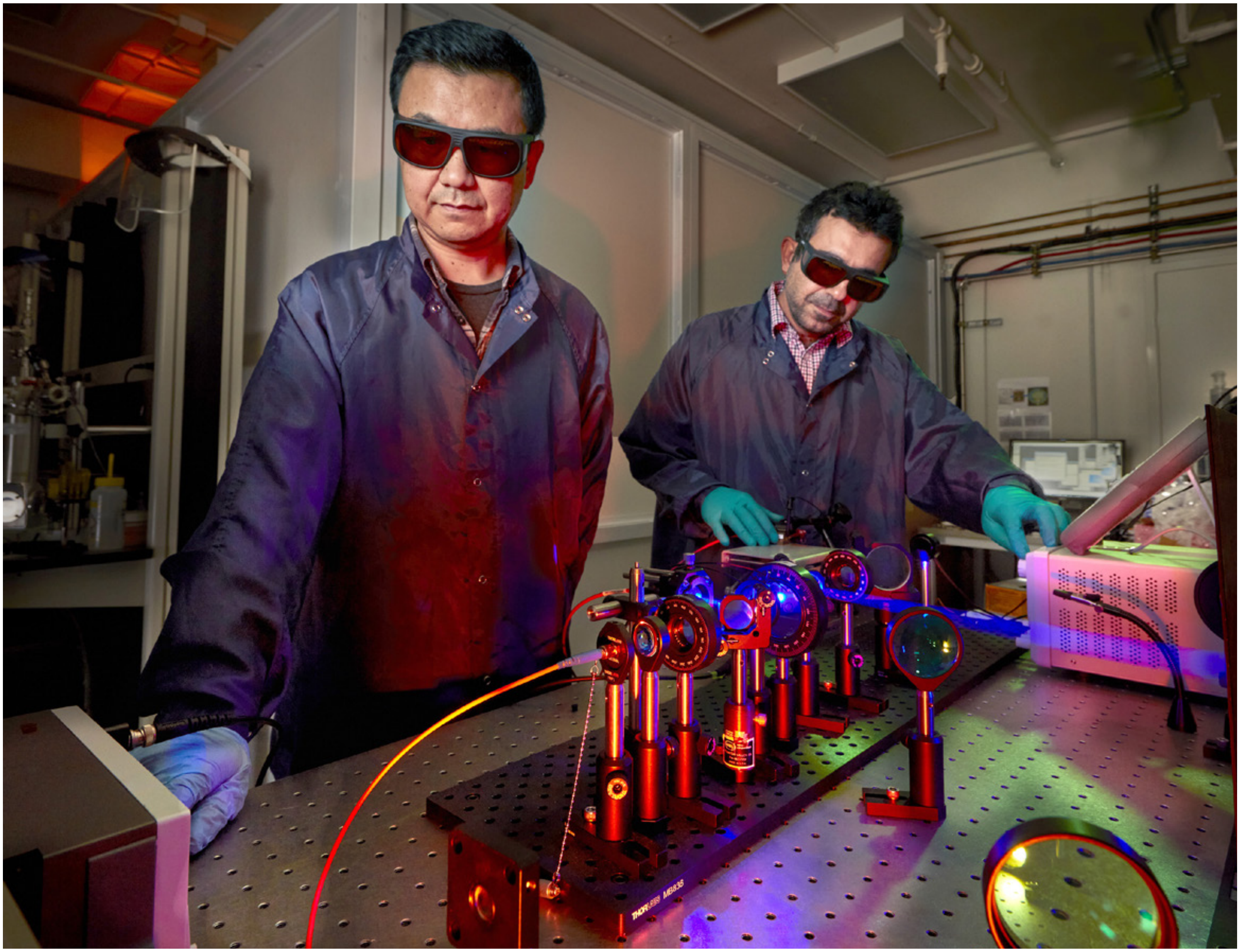
Frye, who came from a semiconductor background before joining the Laboratory, enjoys the interdisciplinary nature of the work that is part semiconductor, part microfluidics, and part optics. “Livermore has so much expertise in one place,” says Frye.

Since the project started, the team has characterized a range of commercially available and emerging–research-grade WBG and UWBG photoconductors for potential applicability to building both high-peak and high-average-power OALVs. Key material properties including photoresponsivity at different wavelengths, resistivity in total darkness, and available and potential wafer size were characterized and input into a technology computer-aided design model to evaluate their suitability. Further, materials were evaluated for LiDT with silicon carbide, aluminum nitride, and gallium oxide meeting a 1 Joule/centimeter-squared (J/cm^2) threshold and a 2 J/cm^2 goal.

Although gallium oxide possesses the most desirable LiDT, the required pump light wavelengths to achieve efficient operation for the material are in the UV and deep UV (DUV) range (280 nanometers), while silicon carbide and aluminum nitride can operate efficiently in the blue or near UV ranges. Long term, Voss’s team has targeted demonstration of a gallium oxide OALV pumped with DUV light for potential future use in high fluence applications. For near-term adoption for NIF’s programmable spatial shapers (PSSs), silicon carbide or aluminum nitride are more attractive options given the cost, availability, and



The project team has computationally screened thousands of materials, investigating their intrinsic ability to generate a stronger response to photoexcitation. Materials of particular interest to the team—aluminum nitride (AlN), bismuth silicon oxide (BSO), silicon carbide (SiC), and gallium oxide (Ga_2O_3)—are noted in the diagrams above.



Livermore's Qinghui Shao and Soroush Ghaniparsi (left to right) test the functionality of 50-millimeter optically addressable light valves (OALVs). Testing with the smaller wafer size enabled the team to get test results for more materials.

intensity of commercial, off-the-shelf components. Other materials, such as zinc gallium oxide may be even more attractive in the future, but their availability is limited to smaller (1 cm^2 or smaller) sizes available at only a few research institutions.

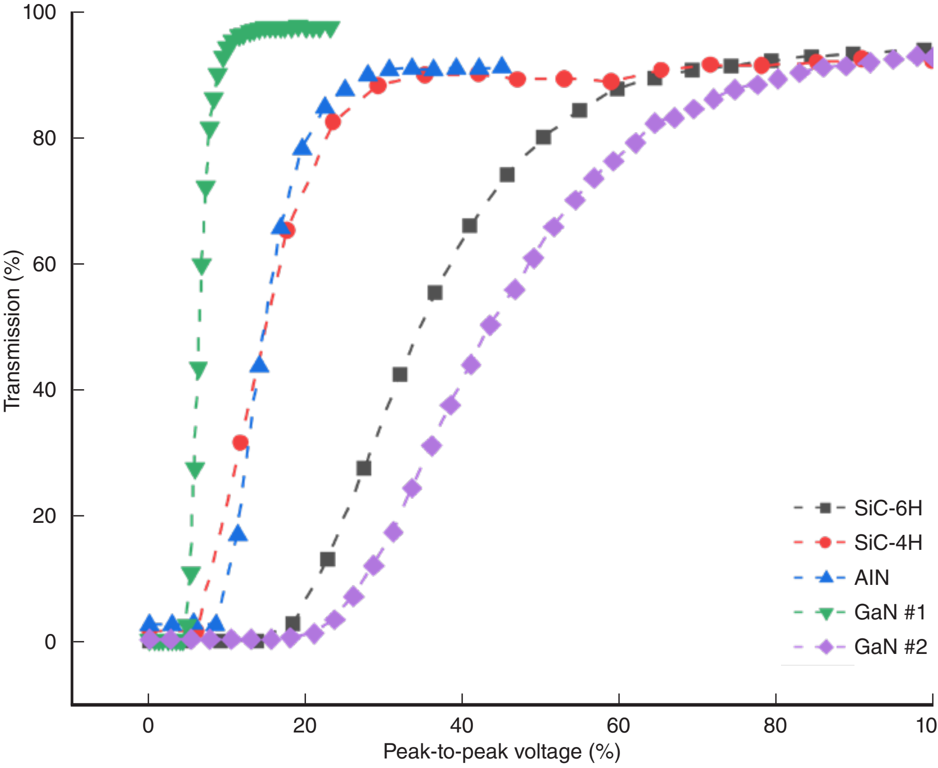
Optimizing OALVs

In the third task, a sub-group focused on building OALVs to maximize performance. Armed with knowledge gained by characterizing candidate dopants and materials, group lead Sara Harrison and device engineer Qinghui Shao used simulation software to design efficient devices, optimizing for different applications. "Our group studied the legacy process to fabricate and test NIF's PSS and adapted the process to our facility, where we address larger-size optics," says Harrison. A testbed was built to understand the performance of one device while others were fabricated.

As part of this task, Frye guided the team in fabricating OALVs using selected UWBG materials. "We've designed the building process and process controls to ensure consistency," says Frye. "Ensuring consistency—particularly when working with coatings in small volumes and 50 millimeter (mm) wafer sizes—is tricky. But the small size enabled us to use different materials." The group has scaled its tooling and design process to achieve a larger, usable area for 100-mm diameter OALVs, increasing the area by a factor of four and increasing device thickness.

The team has already reviewed the performance of several different OALV designs in comparison to the legacy PSS at NIF. At low applied voltage, the fabricated OALVs block 99 percent or greater of the incident light. As voltage is increased, the OALVs operated in gray mode, which describes the case of light partially transmitting. At a high enough voltage or light intensity, the OALVs transition to greater than 90 percent transmissivity. The ratio of blocking to transmitting exceeds 450, well above the requirements for typical OALV applications. All in all, the fabricated OALVs meet performance requirements for NIF and other applications, although continued optimization and refinement of the design and fabrication processes are expected to increase performance further.

Next, the Task 3 sub-group designed OALVs for high average power applications such as diode-based additive manufacturing. In this case, an upper limit on temperature is set by the phase transition of the liquid crystal at around 60°C. At the high average power levels required (5 kilowatts), uncooled bismuth silicon oxide (BSO) OALVs stop functioning within seconds. BSO in particular has extremely low thermal conductivity, making thermal management challenging. By adopting WBG materials with excellent thermal conductivity, such as silicon carbide, heat sinking and active air cooling can be incorporated. The team's designs have undergone further refinement as well as experimental validation of photoconductor heating, and a demonstration device is anticipated to be complete in the next year.



In testing the functionality of OALVs fabricated with a variety of wide bandgap and UWBG photoconductive materials, the team determined that, at low voltage, little to no light passes through the devices (low percentage transmission). As the voltage increases under illumination, they become increasing transmissive—reaching up to 99 percent transmissivity in some cases.

Although the LDRD project is winding down, several transition projects, with both internal and external programmatic customers, have already been launched and are progressing well. In addition to OALVs and other power devices, the team identified promising applications for optoelectronic WBG and UWBG materials. For example, a diamond junction field effect transistor, simulated extensively in the LDRD project, has been selected for negotiation by ARPA–E. Terahertz sources and fast x-ray detectors for NIF have been targeted for proof-of-concept demonstrations. Other possibilities include UWBG radio frequency transistors with no optical triggering.

"This project has broadened our understanding of UWBG materials," says Voss. "Due to the hard work and exceptional progress of the team developing the science and devices initially targeted, we have been able to look into new, related areas. We hope to continue developing and spinning off ideas and technologies to meet Laboratory and broader national needs both now and for the future."

— *Suzanne Storar*

Key Words: bandgap, dopant, Laboratory Directed Research and Development (LDRD), National Ignition Facility (NIF), optically addressable light valve (OALV), ultrawide bandgap (UWBG), wide bandgap (WBG).

For further information contact Lars Voss (925) 423-0069 (voss5@llnl.gov).