

Miniature Optical Sensors for Detection of Water and Air Contaminants

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ISSO RESEARCHERS HAVE INVESTIGATED THE DEVELOPMENT of optoelectronic chemical sensors based on group III-nitride materials. Until recently, compounds of GaN , AlN , InN , and their alloys were known to be optically active from 650 nm (InN) to 200 nm (AlN). Recent results on InN growth and characterization indicate that the bandgap of this material is not 1.9 eV as was previously thought, but 0.7 eV, extending optical applications for these materials to the 1770 nm range. Nitride alloys become thus ideally suited for use in UV-VIS-IR chemical sensors.

Emission and detection devices can be separately tailored to specific wavelengths and grown on the same chip (Fig. 1). Integrated devices made of $AlInGaN$ materials could offer many advantages over current optical chemical sensors, among them high chemical and thermal stability, smaller size, and higher sensitivity.

The objective of this two-year project was to develop and fabricate a working prototype of a nitride-based optoelectronic chemical sensor. The sensor was tested with various concentrations of a known contaminant in water. Towards this goal, the first part of the project has focused on growth of the various materials necessary to fabricate the sensor. In 2000, the ISSO Post-Doctoral Fellow was hired and started working on materials growth issues related to sensor fabrication. Specifically, the growth of high-quality GaN , $AlGaIn$, $InGaIn$, and InN layers on sapphire and Si have been studied. The basic materials research and fabrication and testing of the prototypes were nearly completed in this project with future work directed toward the growth of multi-layer structures and the processing of these samples into devices for testing.

In order to characterize finished sensors, we have recently assembled and tested a portable prototype device that includes “macro” components made from discrete LEDs used as emission sources and photodetectors.

Growth and Characterization of Nitride Materials

The nitride layers in our investigation were grown by radio-frequency gas source molecular beam epitaxy (RFMBE). This method used an EPI Uni-Bulb plasma source to generate active nitrogen species while standard effusion cells supplied the group III metals. As part of our preliminary work, we grew several layers on commercial grade $Si(III)$ substrates which are significantly less costly than sapphire wafers of the same size. Later experiments were performed on sapphire wafers when growth conditions had been narrowed down.

For experiments done on Si substrates during the year 2000,

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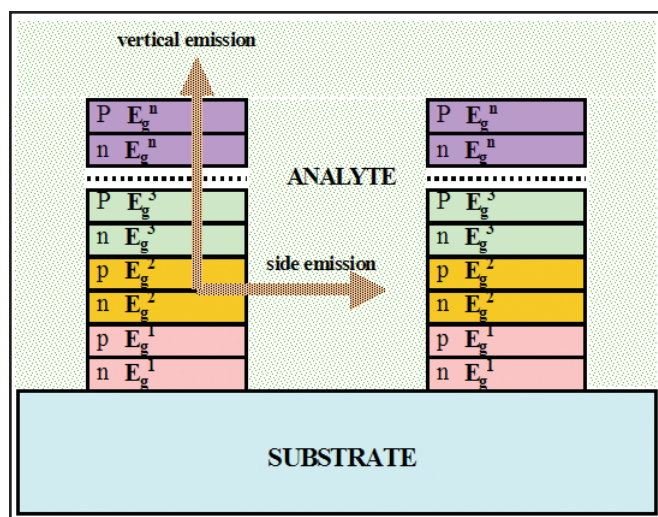


Figure 1. Simplified Structure of a Nano-Integrated Multi-Wavelength Sensor

a 200Å thick AlN buffer layer was deposited between 750°C and 800°C prior to growth of GaN , $InGaIn$, or $AlGaIn$ films.

Experiments on sapphire began with either direct deposition of GaN followed by subsequent layers or by the same AlN buffer layer used for silicon substrates. Since we had previously demonstrated n - and p -type GaN , this work focused on two main objectives: (1) growth of $In_xGa_{1-x}N$ layers with varying values of x for emission and detection windows and (2) growth of $Al_xGa_{1-x}N$ layers for emission wavelengths less than 363 nm. Layers were characterized by photoluminescence (PL), cathodo-luminescence (CL), secondary ion mass spectroscopy (SIMS), and x-ray diffraction (XRD).

A range of substrate temperatures and In/Ga flux ratios were explored to study the effect of growth conditions on $In_xGa_{1-x}N$ layers deposited on Si . Substrate temperature was varied between 600°C and 650°C with a profound impact on the indium incorporation in the film. At 650°C, no indium was found in the layers for any indium flux as determined from PL and SIMS. Only by lowering the growth temperature to 600°C was a substantial amount of indium incorporated into the film. This reaction is caused by the higher re-evaporation rate of In as compared to Ga at these temperatures. By adjusting the ratio of In to Ga during growth, mole fractions of up to 42 percent In were achieved. However, there were problems with uniform indium incorporation. For growths on Si , the indium tended to separate out into two or more distinct compositions of $In_xGa_{1-x}N$.

For experiments performed on sapphire, the growth temperature of 600°C was fixed and the In/Ga ratio was adjusted. Layers grown in this manner showed much less $In_xGa_{1-x}N$ phase separation, as illustrated by the PL data shown in Fig.

2. By changing the relative fluxes, compositions of up to 50 percent indium mole fraction have been achieved without phase separation. The corresponding optical emission for this particular layer is around 520 nm, which is roughly the lower energy (longer wavelength) limit that we should need for our chemical sensors.

The initial investigation on the growth of $Al_xGa_{1-x}N$ for higher energy (lower wavelength) applications was performed on $Si(III)$ substrates. Prior to $AlGaN$ growth at $750^\circ C$, AlN was deposited at $800^\circ C$ followed by GaN at $800^\circ C$. We explored a range of Ga/Al flux ratios to determine the compositional dependence on the group III fluxes.

In the case of $Al_xGa_{1-x}N$, it is the higher sticking coefficient of the Al that strongly determines the film composition. Due to the lattice and thermal expansion mismatches between the layers and the Si substrate, cracking of the films proved a problem. Therefore, layer thickness had to be kept below about 4000\AA in order to prevent cracking during post-growth cooling. Composition of the layers on silicon ranged from 7% Al to 42%, as determined by CL emission peaks, shown in Fig. 3.

Work has recently begun on the growth of $AlGaN$ on sapphire substrates. Because the substrate is transparent, measurement of the transmission of the film as a function of wavelength can be used to determine the bandgap, and, hence, the Al mole fraction of the layer. Only a few growths have been performed to date, but Al compositions of up to 71 percent have been achieved as shown in Fig. 4.

We have made good progress on the development of nitride-based integrated optoelectronic chemical sensors. We have demonstrated growth of $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$ layers by RFMBE on sapphire substrates, with indium mole fractions up to 50% for $In_xGa_{1-x}N$, and $Al_xGa_{1-x}N$, films with up to 71% Al . Currently, we can fabricate layers that are optically active from 200 nm (AlN) up to 520 nm ($InGaN$). The next step in this project will integrate these layers into device structures and fabricate the samples into integrated optoelectronic chemical sensors. That effort will require working closely with personnel at the Johnson Space Center (JSC) in order to test and optimize sensor performance with the goal of being able to accurately detect the concentration of known contaminants in water.

2001-2002 Activity

During 2001-2002, the materials fabrication aspect of this project focused on two main areas. The first area was the growth of $InGaN$, which is the material used as the light-emitting region in our device structure. The purpose was to vary the $InGaN$ growth parameters in order to produce spectral emission in different wavelength regions. Room temperature photoluminescence of the $InGaN$ layers was used to determine the wavelengths of the emission.

The second area of interest was the improvement of the optical and electrical properties of our base GaN material. In order to produce samples with improved properties, film growth parameters, including initialization and deposition conditions, were varied and their effects measured. The resulting films were analyzed by room temperature photoluminescence.

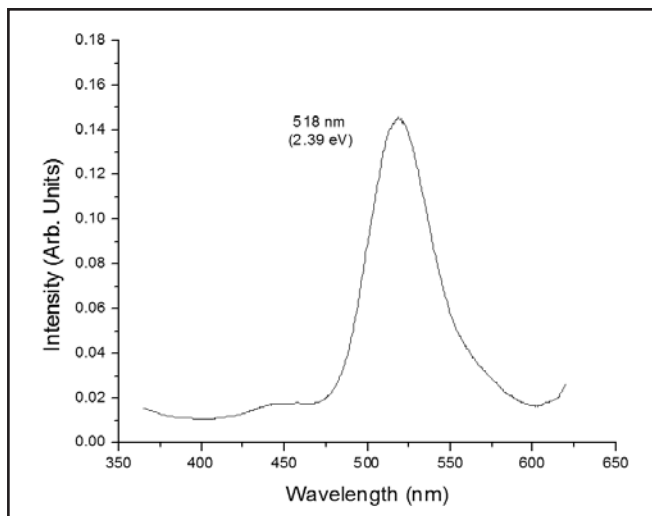


Figure 2. Photoluminescence Spectrum of a $In_{0.5}Ga_{0.5}N$ Layer Grown on Sapphire

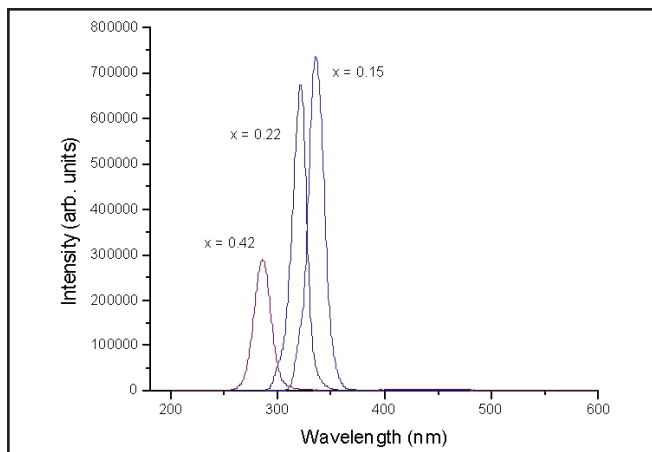


Figure 3. Cathodoluminescence Spectra of $Al_xGa_{1-x}N$ Layers with Compositions Ranging from 15% to 42% Al

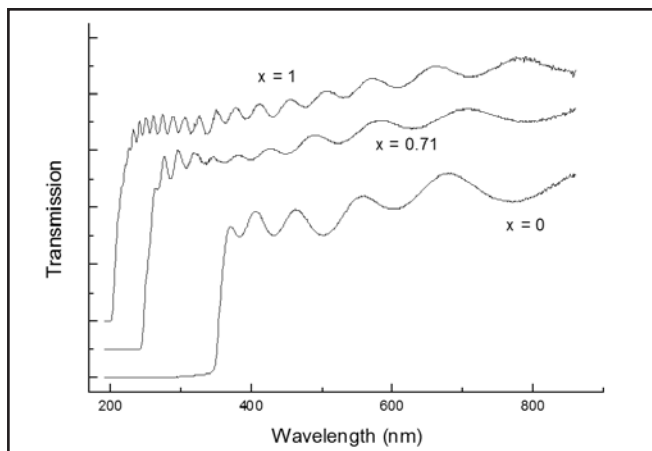


Figure 4. Transmission Spectra from Three Layers Grown on Single-Side Polished Sapphire: GaN , $AlGaN$, and AlN . The adsorption edge of the $AlGaN$ layer is at 239 nm (5.19 eV) which corresponds to a Al mole fraction of about 71%.

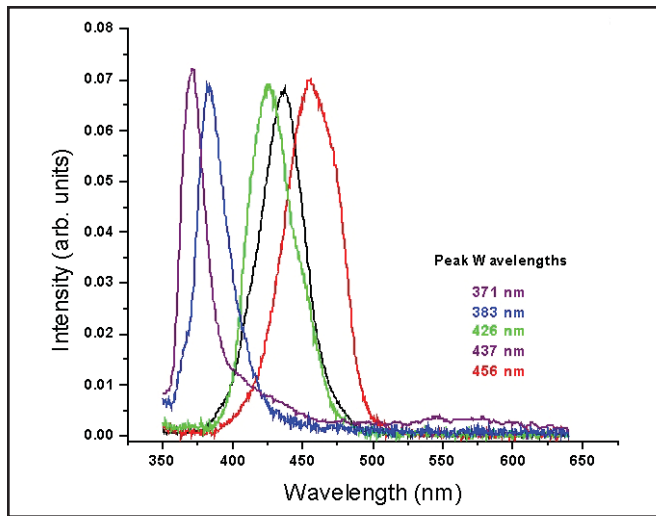


Figure 5. Photoluminescence of Various *InGaN* Layers Emitting at Different Wavelengths

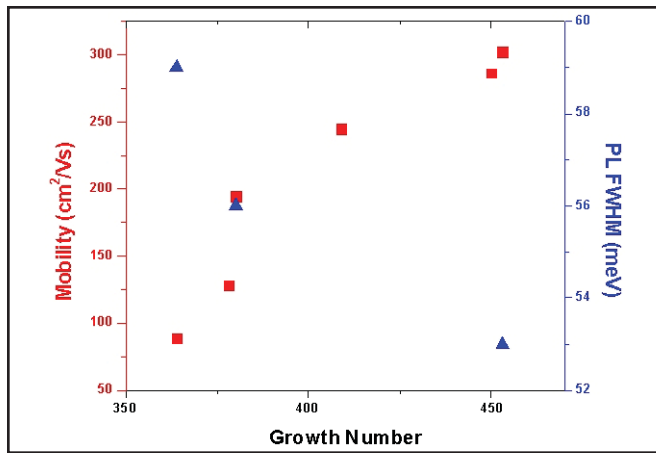


Figure 6. Progression of Si-Doped *GaN* Films Showing Increased Carrier Mobility and Reduced Photoluminescence FWHM Values

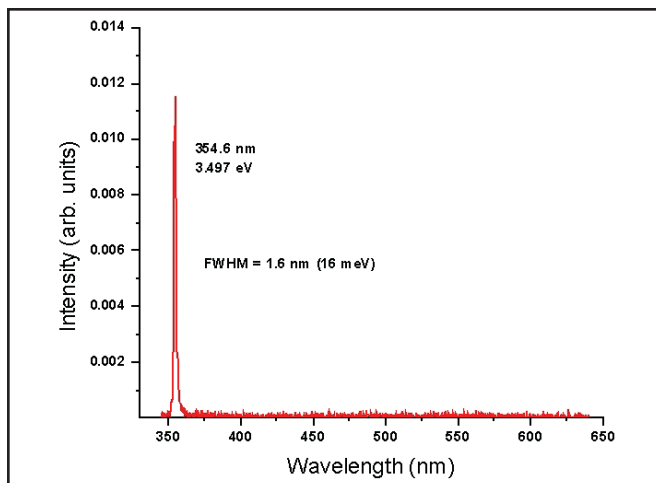


Figure 7. Photoluminescence at 10 K of Typical Improved Si-Doped *GaN* Film Showing Single Peak and Narrow Line Width

cence, low temperature PL, and Hall effect measurements.

Researchers met specific challenges related to each of the two aspects of the project. The growth of *InGaN* is typically more difficult than growth of *GaN* because of the greater vapor pressure of the indium species relative to gallium and aluminum at the film growth temperature. This difficulty necessitates lowering the deposition temperature so that indium can incorporate into the *InGaN* film. The drawback is that the gallium species have less surface mobility at this lower temperature and thus require a lower growth rate. In addition, when growing *InGaN* layers that are several hundred angstroms thick, the indium tends to segregate to the surface of the film, thus leading to uneven indium composition within the layer.

To overcome these problems, we employed a quasi-superlattice structure where the *InGaN* was grown by alternately opening and closing the indium shutter with the gallium and nitrogen shutters always open. This would allow any excess indium left over from the direct growth of *InGaN* to be consumed during the stage when the indium shutter was closed. Control of the indium composition could be obtained by varying both the ratio of indium to gallium and the ratio of time the indium shutter was opened and closed.

One of the issues in *GaN* growth is the lack of lattice-matched substrates on which to grow epilayers. This lack of substrates results in *GaN* layers with large numbers of dislocations which can reduce the optical quality of the material as well as the mobility of the free carriers. In order to address these problems, we optimized the initiation of film growth on the substrate, the deposition of the *AlN* buffer layers, and the growth parameters of the *GaN* overlayers. Mainly, the substrate preparation, buffer layer growth temperature, and buffer layer thickness were varied. The effects on the optical quality were gauged by the full width at half maximum (FWHM) of the room temperature photoluminescence and the electrical quality judged by measuring the free carrier mobility using the Hall effect.

For the growth of *InGaN*, we were able to demonstrate films that were optically active from 371 nm to 456 nm, as shown in the room temperature photoluminescence in Fig. 5. The emission from the films was typically single-peaked, which indicates that segregation of the indium during the growth was mostly avoided. The layers were grown with indium/gallium flux ratios from 0.72 to 1.11 and *In + Ga / Ga* shutter ratios from 1 to 0.72.

In the case of the base *GaN* materials, we were able to achieve layers with improved electrical and optical properties. As the left axis of Fig. 6 illustrates, the electron mobility of similarly doped *GaN* films was increased from 88.5 cm^2/Vs to over 300 cm^2/Vs . At the same time, the optical quality was improved, as shown on the right axis of Fig. 6, by the reduction of room temperature PL FWHM values from 59 meV to 53 meV. In addition to room temperature measurements, our better layers exhibited excellent photoluminescence at 10 K. Figure 7 is an LT PL example of a layer with very bright near-band-edge emission at 354.6 nm with a narrow FWHM of 16 meV. The low temperature result is further indication of the optical quality of the recent films.

Activity in 2003

The main focus of the nitride material growth during the year 2003 was investigation of conditions for the growth of semiconductor quality *InN* layers. The ultimate goal of this work is to extend further into the IR range the spectral range of the optical components based on III nitrides.

InN has been much less studied than other III-Nitride materials, such as *GaN* and *AlN*. The reason is the difficulty of growing highly crystalline *InN*. *InN* has a large lattice mismatch with *GaN* (11%) and *AlN* (14%), which are typically used as buffer or template layers,

and with the typical substrate materials Al_2O_3 (26-29%) and *Si*(III) (8%). In addition, *InN* is less thermally stable than the other nitrides and usually has a high background *n*-type doping level attributed to likely nitrogen vacancies.

Recent results in the growth of *InN* by RF-MBE¹⁻⁴ have brought a better perspective to this material and highlighted some of its potential advantages. *InN* has a very high room temperature electron mobility ($>2000\text{ cm}^2/\text{Vs}$), has higher polarization and piezoelectric constants than *GaN*, and, most important, has been found to have a much lower bandgap than was predicted and measured earlier from lower quality films. The new bandgap measuring $\sim 0.7\text{--}0.9\text{ eV}$ for *InN* has not been universally accepted. There is however strong evidence from the multiple literature reports and our laboratory that the bandgap is not the previously-thought 1.9 eV. Thus, alloys between *GaN*, *AlN*, and *InN* have the theoretical potential to cover a very large spectral range, from 200 nm up to 1.38-1.77 μm .

The films detailed in these recent reports have all been fabricated by RF-MBE employing *InN* grown on templates of *GaN* and/or LT-*InN* in a growth temperature range between 370°C-600°C. In these reports, the intrinsic background carrier concentration has been reduced from typical values of 10^{20} cm^{-3} down the low 10^{18} cm^{-3} and even 10^{17} cm^{-3} ranges. Both room and low temperature band edge-related luminescence have been observed. Factors such as buffer layer type, growth temperature, and template polarity play major roles in the optical and electrical properties of the layers.

Our preliminary work on the growth of *InN* has demonstrated that we are able to grow smooth, two-dimensional *InN* films on *GaN* buffer layers deposited on sapphire substrates. We have seen a very strong growth temperature and buffer layer polarity dependence in our growths, with the best results so far employing a growth temperature around 500°C. We have observed 14 K photoluminescence in the energy range 0.71 to 0.73 eV (un-calibrated response) from non-optimized, 2000Å thick *InN* films (Fig. 8).

Future work has been directed toward further improvement

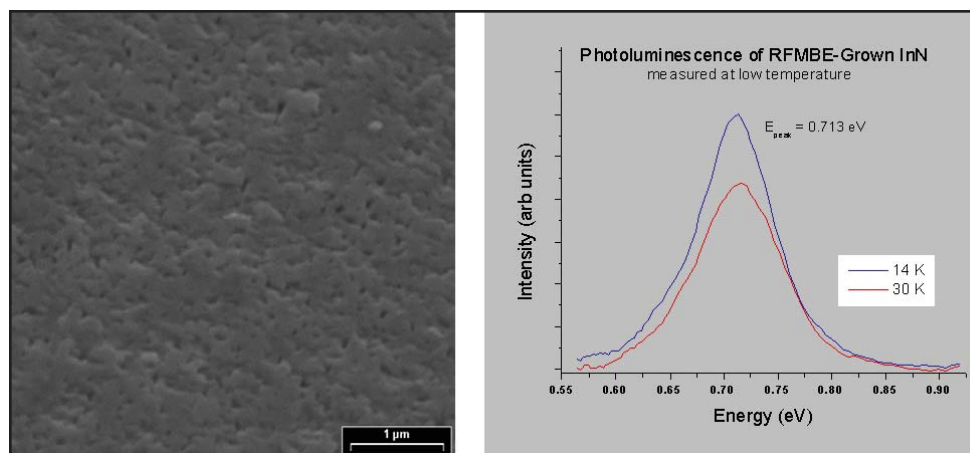


Figure 8. *InN* Grown on Sapphire: SEM View of the Surface (l) and Low Temperature Photoluminescence (r)

of the *InN* growth by employment of a large variation of growth substrates, substrate preparation, and growth parameters in order to investigate their applicability for Schottky barrier diode fabrication.

Fabrication and Testing of the Portable Optoelectronic Sensor (POS-1) Prototype

The new POS-1 device prototype was developed from vacuum-grown nitride thin-film technology at the Texas Center for Superconductivity and Advanced Materials (TCSAM). An Optical Multifunctional sensor (Fig. 9) has been integrated into a working biomedical instrument in collaboration with Integrated Micro Sensors, Inc. The instrument was operated and tested in the field as part of a Mars Society simulation called the Mars Analog Research Station (MARS) project. The second field season of the MARS project included a Mars base-like habitat located in the desert of the American southwest. In this Mars-like environment, the MARS Society has executed a program of extensive long-duration geology and biology field exploration operations conducted in the same style and under many of the same constraints that they would encounter on the Red Planet.

See <http://www.mars.society.org/mdrs/index.asp>.

In a double-blind test, the instrument was used to analyze water at the simulation site and returned to TCSAM/IMS with the analyte water for laboratory verification. Data obtained under carefully controlled conditions at TCSAM matched samples gathered in the Utah desert. In the simulation, the sensor proved both durable and easy to use, operating optimally in extreme conditions, in the hands of technicians/"astronauts" generally unfamiliar with the system. The ultimate usefulness (and marketability) of the sensor system depends on a library of environmental chemical signatures. The water used in the simulation and subsequent in-house testing is undergoing further bio-analysis at UH, representing the first action toward building a referential database for the logic protocols of the sensor.



Figure 9. Portable Optoelectronic Sensor (POS-1)

References

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Publications

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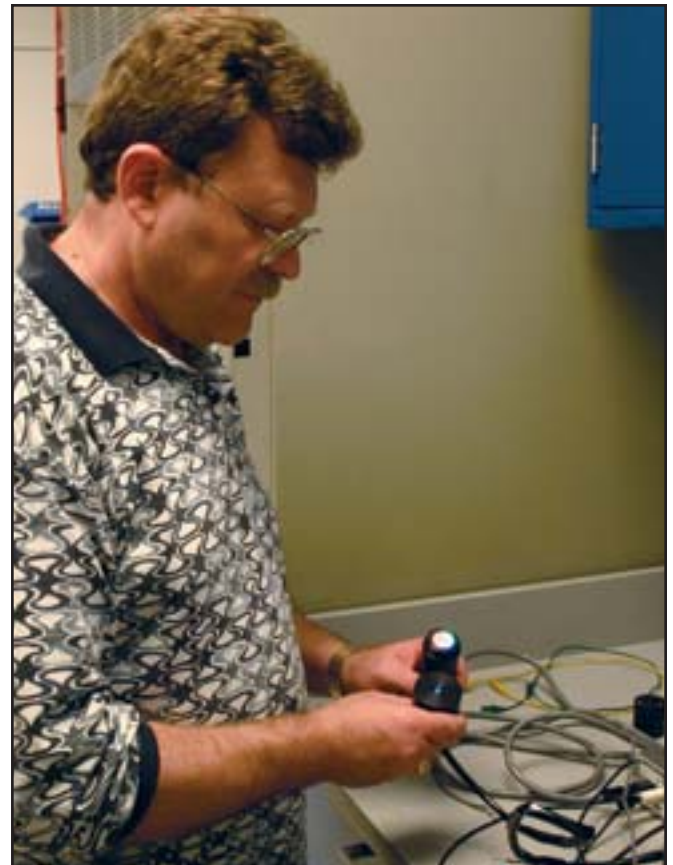
Starikov, D., C. Boney, N. Medelci, R. Pillai, and A. Bensaoula. "Dual-Color UV/IR Photodiodes Based on *AlGaIn* Grown on *Si* and SOS for Advanced Fire/Flame Detectors," *Proc., 50th International AVS Symposium* Baltimore, MD, Nov. 21-26, 2003. 133.

Presentations

Starikov, D. "Employment of III-Nitride Materials for Microsensor Applications," Seminar, Texas Center for Superconductivity and Advanced Materials, University of Houston, Houston, TX, Feb. 21, 2003.

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Starikov, D., C. Boney, N. Medelci, R. Pillai, and A.



PORTABILITY—Dr. David Starikov, researcher in TCSAM Laboratories, conducts research on the portable optoelectronic sensor designed to detect bio-chemical substances by measurements of absorption, fluorescence, and scattering. He has lectured and published on the use of advanced optical sensors for detecting fire and flames.

Bensaoula. "Dual-Color UV/IR Photoiodes Based on *AlGaIn* Grown *Si* and SOS for Advanced Fire/Flame Detectors," Fiftieth International AVS Symposium, Baltimore, MD, Nov. 21-26, 2003.

Funding and proposals

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