

Compact and highly-integrated chemical and biological sensors based on waveguided chalcopyrite heterostructures

N. Dietz ^{a,b}, D. P. Krivoschik ^b and F. L. Madarasz ^b

May 2, 2002



a) Georgia State University
Department of Physics & Astronomy
29 Peachtree Center Avenue, Science Annex, Suite 400
Atlanta, GA 30303

<http://www.phys-astr.gsu.edu>



b) Xoetronics, LLC
113 Wertsville Road
Ringoes, NJ 08551

<http://xoetronics.com>



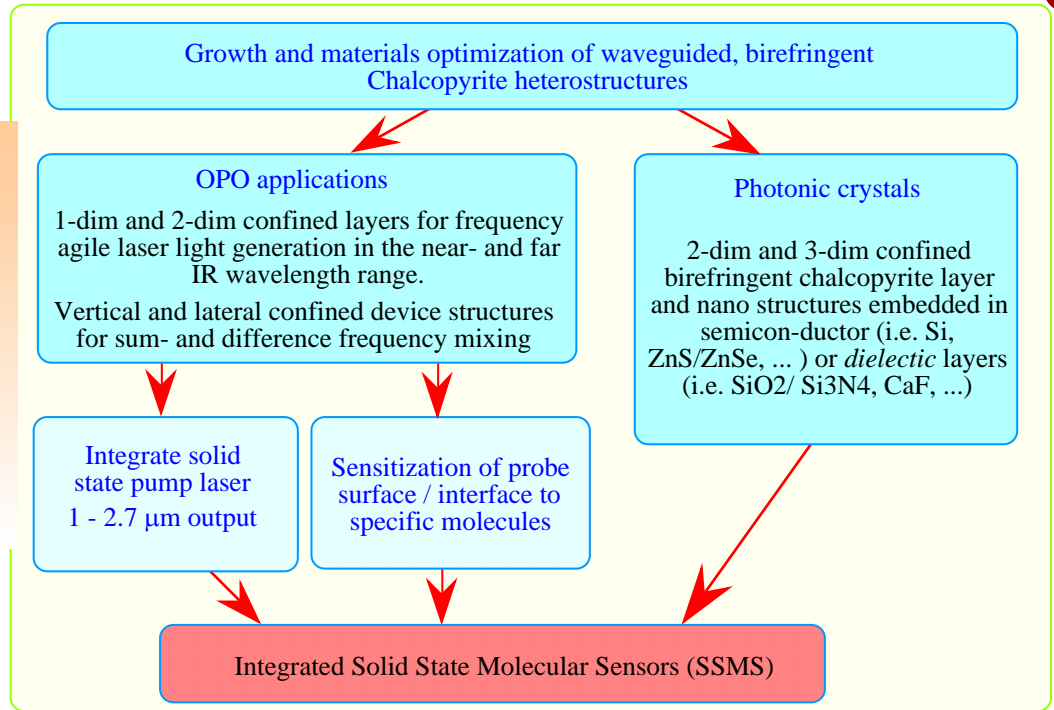
Solid-State Molecular Sensor (SSMS) systems are based on a unique, patented, optically confined birefringent, chalcopyrite (CP) heterostructure technology. It identifies target chemicals and biological molecules, *real-time* under ambient conditions. SSMS waveguided heterostructures have a spectral wavelength range and tunability which enables the discrimination and identification of a vast cross section of molecular structures by using resonant phase-and/or amplitude sensitive detection.

The SSMS technology *miniaturized* and integrated with existing Si and III-V compound semiconductor technology provides numerous potential *real-time* applications. For example: quick and remote screening of air pollutants; recognition of chemical/biological (CB) hazards in the environment, monitoring of surface corrosion/etching processes; as well as bio-medical testing and drug development.

The SSMS technology satisfies the essential criteria for compact, integrated CB detection systems that focus on localized detection. The criteria that must be addressed are:

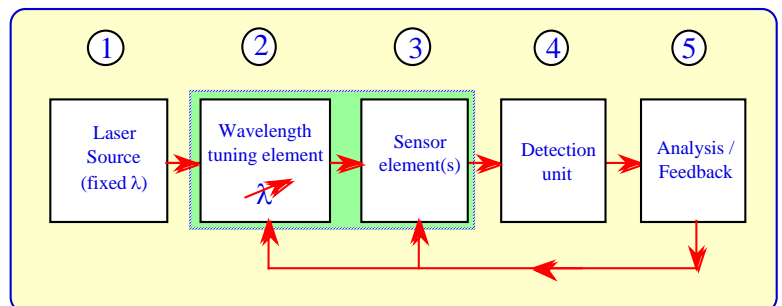
- 1) High sensitivity /low detection limits;
- 2) Capability to discriminate between multiple targets of interest;
- 3) Self-calibration and adjustable warning and alarm thresholds;
- 4) Robust maintenance and easily exchangeable modules;
- 5) Operational at ambient and hazardous environmental conditions;
- 6) Low power consumption;
- 7) Functional reliability/long life;
- 8) Portable; and,
- 9) User Friendly.

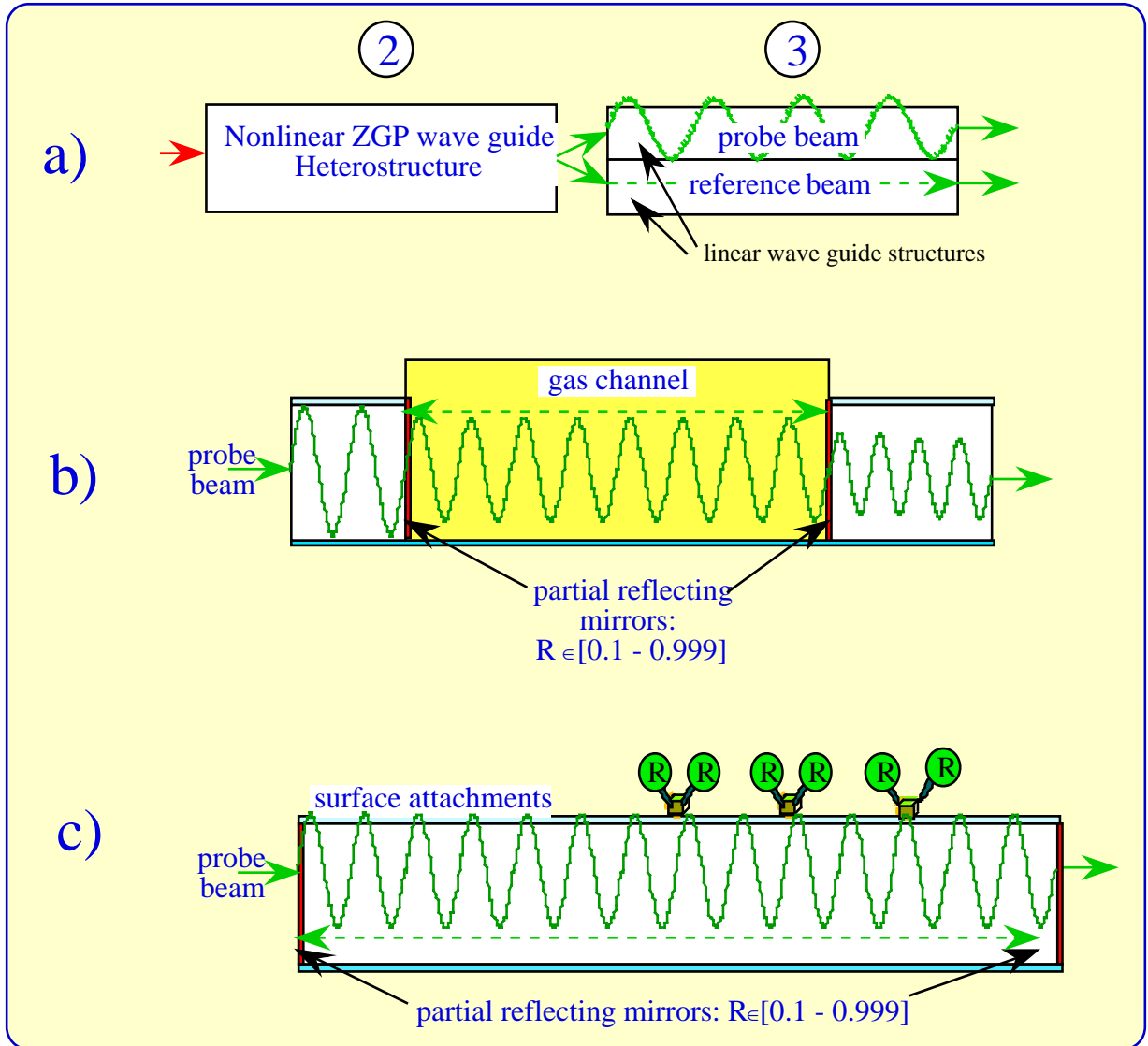
Potential fields of applications for optically confined birefringent $Zn(Ge_{1-x}Si_x)P_2$ heterostructures.



The fundamental operational characteristic of the SSMS lies in its extreme sensitivity to surface changes in the presence of CB target elements of interest residing on a test surface. The surface is probed by an evanescent electromagnetic wave propagating in a waveguided channel just below the surface. Any change in surface properties induces amplitude and phase shifts in the wave. This wave is coupled *nonlinearly* to another wave propagating in an adjacent, birefringent waveguide(s), which modifies the spectrally the phase matching conditions for frequencies generated in an optical parameter oscillator (OPO) process. In this nonlinear OPO process, *small spectral phase and amplitude shifts are translated in large frequency shifts*, that are much easier and more reliable to analyze than amplitude variations. The wide nonlinear optical transparency range [$2\text{ mm} < l < 10\text{ mm}$ for $Zn(Ge_{1-x}Si_x)P_2$] allowing for the characterization of a vast selection of CB-agents with increased sensitivity and accuracy of discrimination.

Principle of an integrated sensor arrangement:

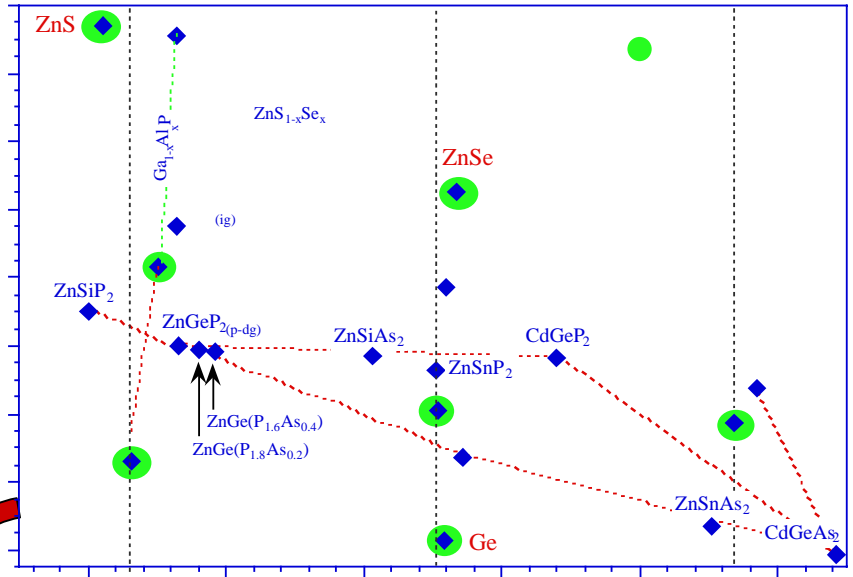




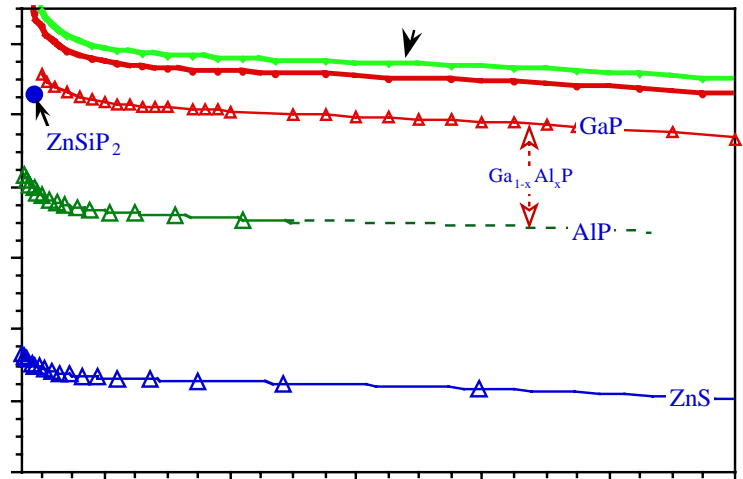
a) schematic of (2) and (3), where the sensor probe area is formed by two linear wave guides, the probe beam and the reference beam.

b) and c) are two viable embodiments for probing a gas volume and for probing surface attachments, respectively. By using partially reflecting side face, multiple internal reflectance conditions are used to enhance the sensitivity of the sensor.

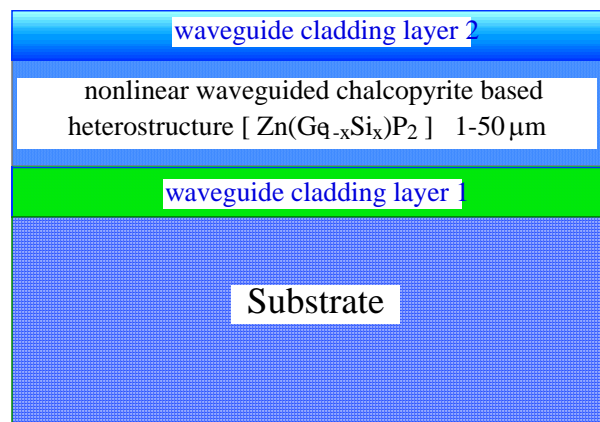
Integration with Si based electronic circuitry favors lattice-matched growth of $ZnSi_xGe_{1-x}P_2$ heterostructures.



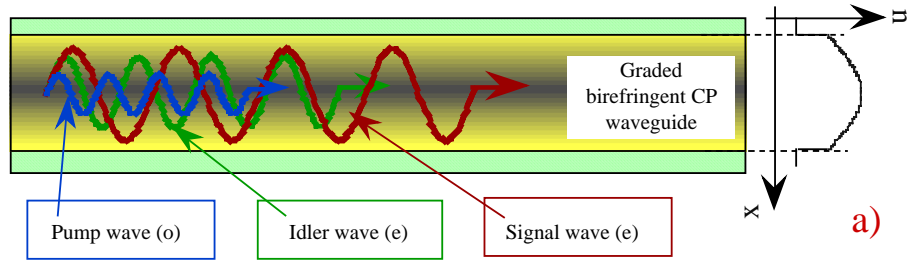
Potential lattice-matched cladding layers for $ZnSi_xGe_{1-x}P_2$. Ternary alloys of $Ga_{1-x}Al_xP$, $ZnS_{1-x}Se_x$ allow refractive index tuning and the engineered coupling between birefringent layers.



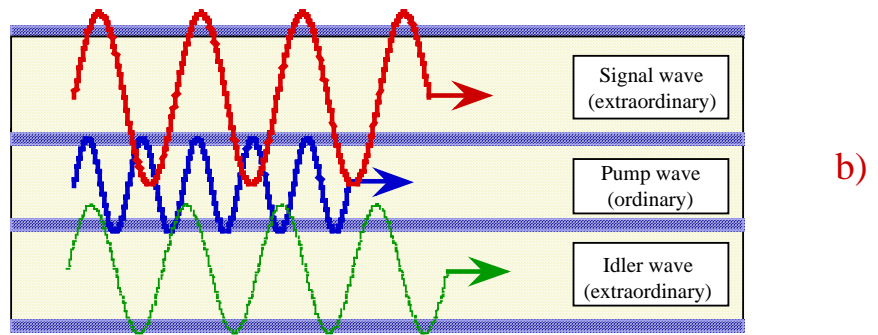
Design and optimization of waveguided heterostructure



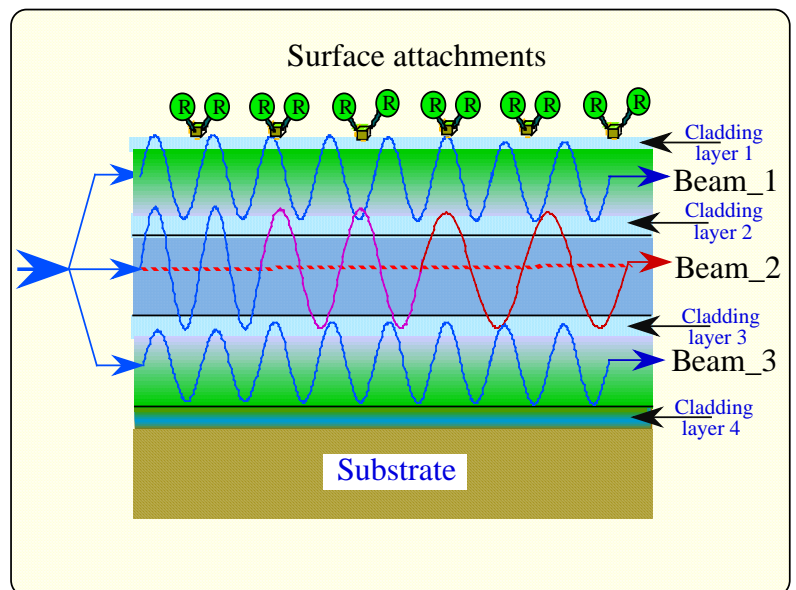
Schematic of sensing element based on nonlinear optical interactions in a graded nonlinear waveguide.



(a) an optical confined single CP structure, and
(b) optical coupled, multiple CP heterostructures



Schematic of a differential sensor configuration using multiple layered linear / non-linear waveguided heterostructures to characterize surface attachments.



The SSMS development critically depends on advances in material growth optimization, an improved understanding of materials defect chemistry and the quality of heterostructural interface formation. The development will also require the formation of interdisciplinary teams working together on predictions, simulations, growth, materials characterization and device design aspects.

Development steps for surface-activated biological & chemical sensors based on waveguided, birefringent CP structures operating in the wave-length region $2 \mu\text{m} < \lambda < 10 \mu\text{m}$:

- *Optimize the growth of waveguided heterostructures,*
- *Characterization of structural and optical layer quality,*
- *Develop theory and modeling of nonlinear electromagnetic*

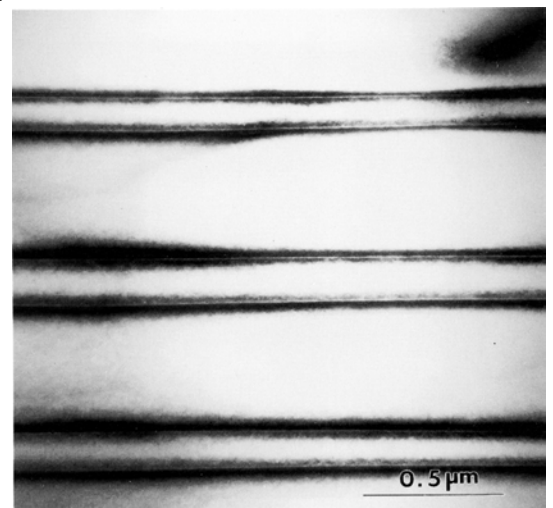
(EM)

waves interactions in coupled optically confined layers,

- *Develop theory and models for EM interactions with surface adsorbates (e.g. molecules and/or complex biological groups),*
- *experimental validation of nonlinear EM wave propagation, and*
- *feasibility studies on planar prototypes.*

Example:

Cross-sectional TEM bright field image of a multiple GaP / ZnGeP₂ heterostructure grown on a (001) GaP substrate [after ref. 4].





Growth and integration challenges with existing opto-electronic technology

Even though the growth of embedded GaP / ZnGeP₂ / GaP multiple heterostructures has been demonstrated, further extended research efforts are need in:

- *the nano-scale controlled layer growth by organometallic chemical vapor deposition (OMCVD);*
- *the development and optimization of "thick-layer" growth techniques such as liquid phase epitaxy (LPE);*
- *the real-time controlled growth of index-graded birefringent layers and their optical/electrical confinement layers;*
- *the characterization and understanding of defect chemistry; and,*
- *the characterization of layer quality and their nonlinear properties.*

The main advantage of the compound semiconductor ZnSi_xGe_{1-x}P₂ is the lattice-match to Silicon, enabling compact, monolithically integrated sensor structures.

This integration task has to address the growth of Si / ZnSi_xGe_{1-x}P₂ / Si and/or GaP multiple heterostructures. Large-area (up to ø 12"), high-quality Si substrate wafers are ready available, enabling multi-area sensors and/or integrated sensors at reasonable costs.

However, the growth of such structures is challenged by *"the formation of abrupt interfaces"* - also known as *"inter-diffusion problem"*. *The problem can be addressed by* paying close attention to surface chemistry (heteroepitaxial nucleation process) and integrating of real-time growth diagnostic and growth control.

Integration with existing III-V opto-electronic structures favors a second CP system: Zn(Ge_{1-x}Si_x)As₂ on GaAs, which has the potential for a complete monolithic sensor system. However, more needs to be known about the growth and the material properties of such heterostructures.

Example:

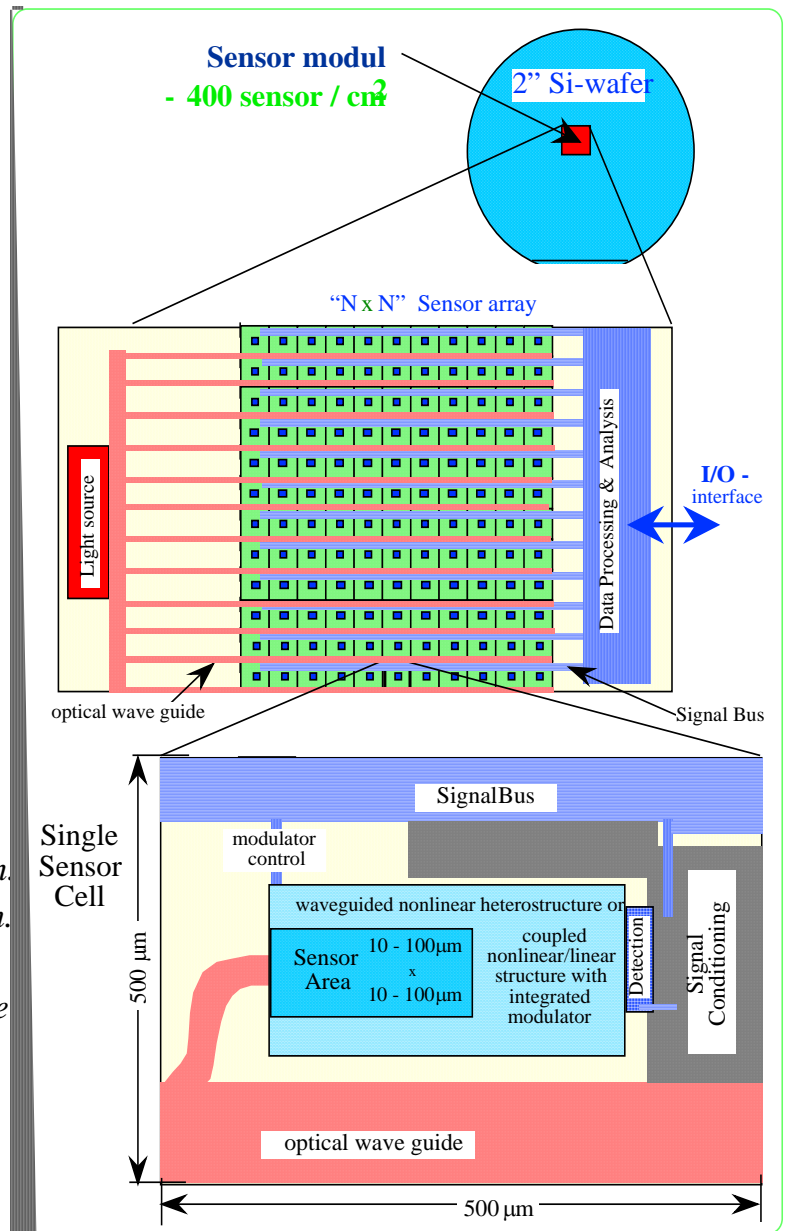
**Concept of a multi-area
Solid-State Molecular
Sensor (SSMS)
arrangement for rapid
drug testing / screening.**

Advantages:

- Large-area Si wafers (up to ϕ 12") readily available.
- Use / Integration of Si-technology and device knowledge.
- High sensitivity due to nonlinear gain.
- Tuning of probe light from 1 - 10 μm .
- Spectral sensing.
- Probe geometry easily tailored in size to specific problem.

Impact:

- Noninvasive testing of drugs (*No chemical markers required!*).
- Studies of the dynamics of chemical/biological reactions in *Real-Time*.
- Noninvasive, real-time studies of surface corrosion and etching processes.
- Enabling a compact, portable sensor concept for:
 - *environmental hazard screening;*
 - *chemical pollution monitoring; and*
 - *biological / medical applications.*



- ✓ Unique nonlinear optical interactions in waveguided heterostructures for frequency tuning in the IR-wavelength regime.
- ✓ Characterization of light beam interactions in coupled nonlinear waveguides.
- ✓ Applications towards molecular specific CB-sensors.

The Solid-State Molecular Sensor (SSMS) technology can be miniaturized to the size of a matchbook with potential applications for:

- ✓ quick, remote screening and recognition of chemical hazards in the environment;
- ✓ continuously and rapidly monitoring of trace impurities; related to air/water pollution;
- ✓ real-time monitoring of surface corrosion/etching processes; and,
- ✓ operations in ambient and hazard environments.

SSMS's will have a worldwide economic and technological impact when used in the detection of CB agents, as well as for a variety of medical sensing applications, such as for the identification and monitoring of complex biological structures, testing for allergic reactions and screening for common diseases. Moreover, the SSMS will hasten the time of development and introduction into the marketplace of critically needed drugs by the monitoring of biochemical and molecular cellular responses to the candidate drugs.

References:

- 1) "Chalcopyrite based nonlinear waveguided heterostructure devices and fabrication and operating methods" N. Dietz US Patent Application Serial No. 09/501,401, Notice of Allowance mailed March 21, 2002.
- 2) "Chemical and Biological Sensors based on optically confined birefringent chalcopyrite heterostructures" N. Dietz and F. L. Madarasz, [Preprint: <http://www.phy-astr.gsu.edu/dietz/publications.html> or <http://xoetronics.com/technology.htm#SSMS>] (2002).
- 3) "Native defect related optical properties of ZnGeP_2 ", N. Dietz, I. Tsveybak, W. Ruderman, G. Wood and K. Bachmann, Appl. Phys. Lett. **65** (22) p. 2759-62 (1994).
- 4) "GaP/ZnGeP₂ Multiple Heterostructure", G.C. Xing and K.J. Bachmann, J. Crystal Growth **147**(1/2), pp. 35-8 (1995).
- 5) "Organometallic chemical vapor deposition and characterization of $\text{ZnGe}_{1-x}\text{Si}_x\text{P}_2$ -Ge alloys on GaP Substrates", G. C. Xing, K. J. Bachmann, J. B. Posthill and M. L. Timmons, J. Crystal Growth **113**, p.113-119 (1991).
- 6) "Organometallic Chemical Vapor Deposition of Epitaxial ZnGeP_2 Films on (001) GaP Substrates", G.C. Xing, K.J. Bachmann, G.S. Solomon, J.B. Posthill and M.L. Timmons, J. Crystal Growth **94** p. 381 (1989).