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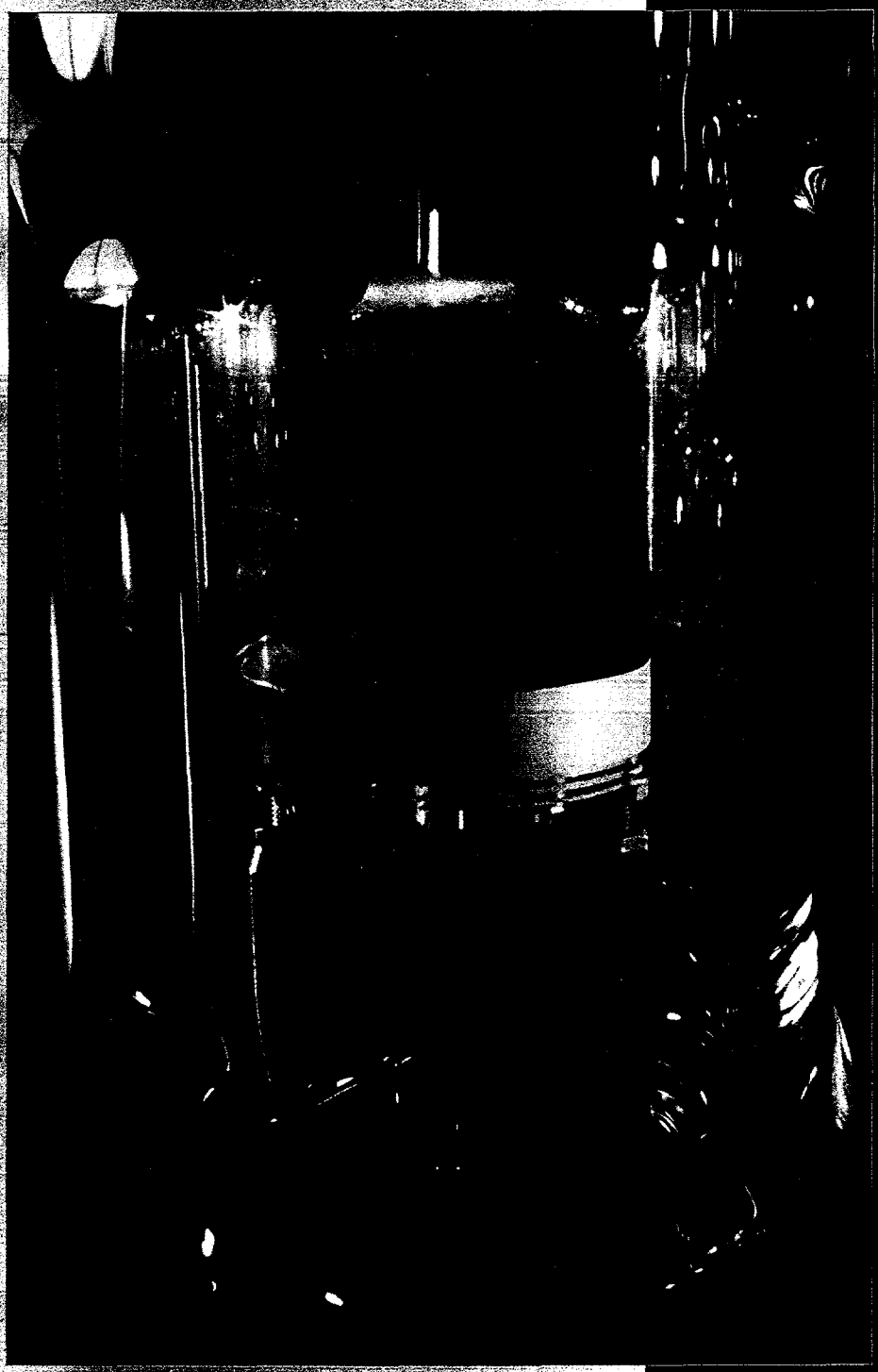
CHEMICAL VAPOR DEPOSITION SCIENCES



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Sandia National Laboratories is a multiprogram laboratory operated under contract DE-ACD476DP00789 for the United States Department of Energy (DOE). Sandia is one of the largest engineering research and development laboratories in the United States, with major facilities at Albuquerque, New Mexico and Livermore, California.

Sandia's primary responsibilities are research and development of nuclear weapon systems from concept to retirement. Additionally, Sandia has extensive responsibilities in other areas of national importance. These include energy research, microelectronics, technology transfer, fusion energy, reactor safety and nuclear safeguards.

This brochure provides basic information on Sandia's capabilities in the physical and chemical sciences of Chemical Vapor Deposition (CVD) and related materials processing technologies. It contains a brief description of the major scientific and technical capabilities of the CVD staff and facilities, and a brief discussion of the approach that the staff uses to advance the scientific understanding of CVD processes. For further information, write or call Sandia at the address listed in the back of this booklet.

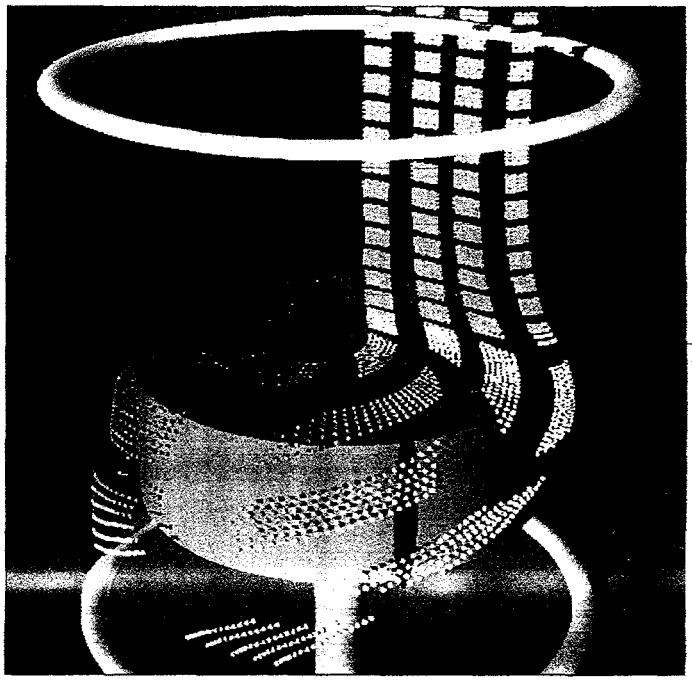
CHEMICAL VAPOR DEPOSITION (CVD) SCIENCES AT SANDIA NATIONAL LABORATORIES

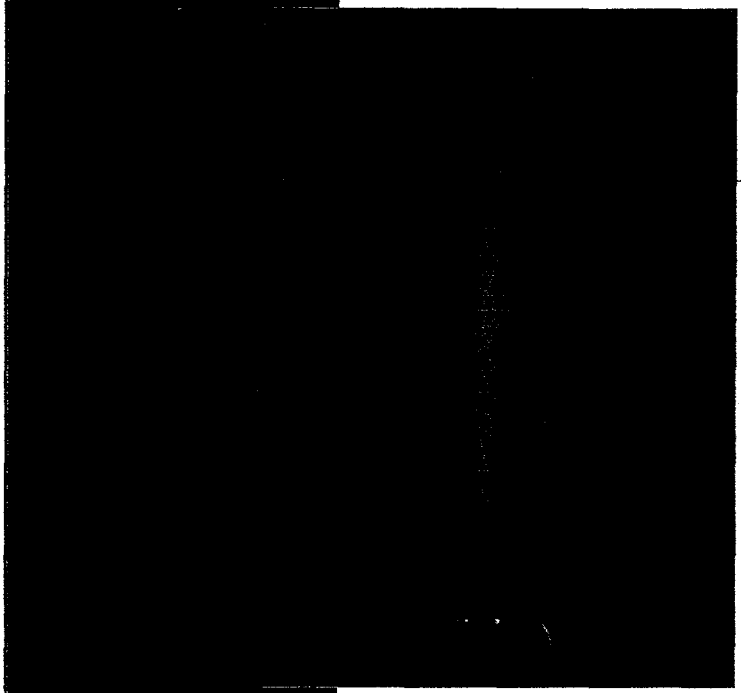
Chemical vapor deposition (CVD) is a widely used method for depositing thin films of a variety of materials. Applications of CVD range from the fabrication of microelectronic devices to the deposition of protective coatings. New CVD processes are increasingly complex, with stringent requirements that make it more difficult to commercialize them in a timely fashion. However, a clear understanding of the fundamental science underlying a CVD process, as expressed through computer models, can substantially shorten the time required for reactor and process development.

Research scientists at Sandia use a wide range of experimental and theoretical techniques for investigating the science of CVD. Experimental tools include optical probes for gas-phase and surface processes, a range of surface analytic techniques, molecular beam methods for gas/surface kinetics, flow visualization techniques and state-of-the-art crystal growth reactors. The theoretical strategy uses a structured approach to describe the coupled gas-phase and gas-surface chemistry, fluid dynamics, heat and mass transfer of a CVD process. The software used to describe chemical reaction mechanisms is easily adapted to codes that model a variety of reactor geometries. Carefully chosen experiments provide critical information on the chemical species, gas temperatures and flows that are necessary for model development and validation.

Computer simulation shows ideal gas flow pattern in a rotating disk reactor.

Laser-induced fluorescence shows gas mixing in the flow pattern from a concentric multi-gas injector.





A tunable laser system is used to probe the gas phase in a research rotating disk CVD reactor.

EXPERIMENTAL CAPABILITIES

Research CVD Reactors

A major challenge in understanding commercial CVD reactors is to model simultaneously both the complex chemistry and the complex fluid flow. Sandia scientists have developed research CVD reactors to expedite model development. The use of simple geometries facilitates the task of separating the effects of heat and mass transfer from the effects of chemical reactions. The reactors, which include horizontal flow cells and rotating disk reactors, are specifically designed to provide good optical access.

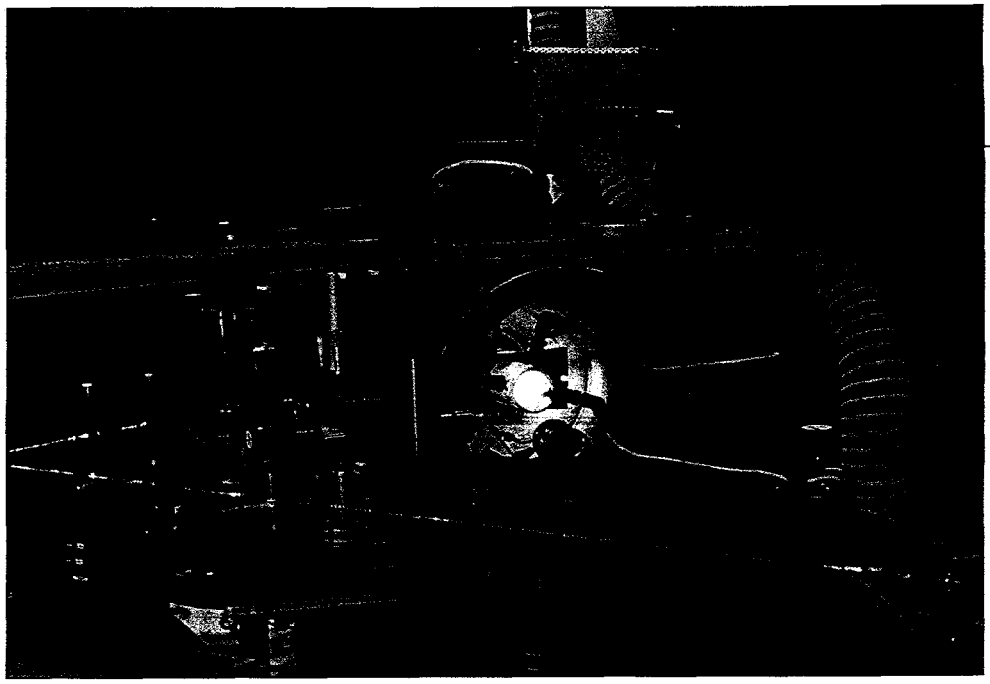
Flow Visualization

Flow visualization of gas-flow patterns in CVD systems is useful for studying recirculation patterns, gas injection and gas mixing, and for confirmation of fluid-mechanical models. CVD scientists have used laser-light scattering from particles seeded in the gas flow to study flow patterns in a rotating disk reactor, UV absorption of non-fluorescing reactants in a channel-flow reactor, and imaging of laser-induced fluorescence to examine gas mixing for a concentric injector. Scattering of laser light is also useful as a detector of particulates in process gases.

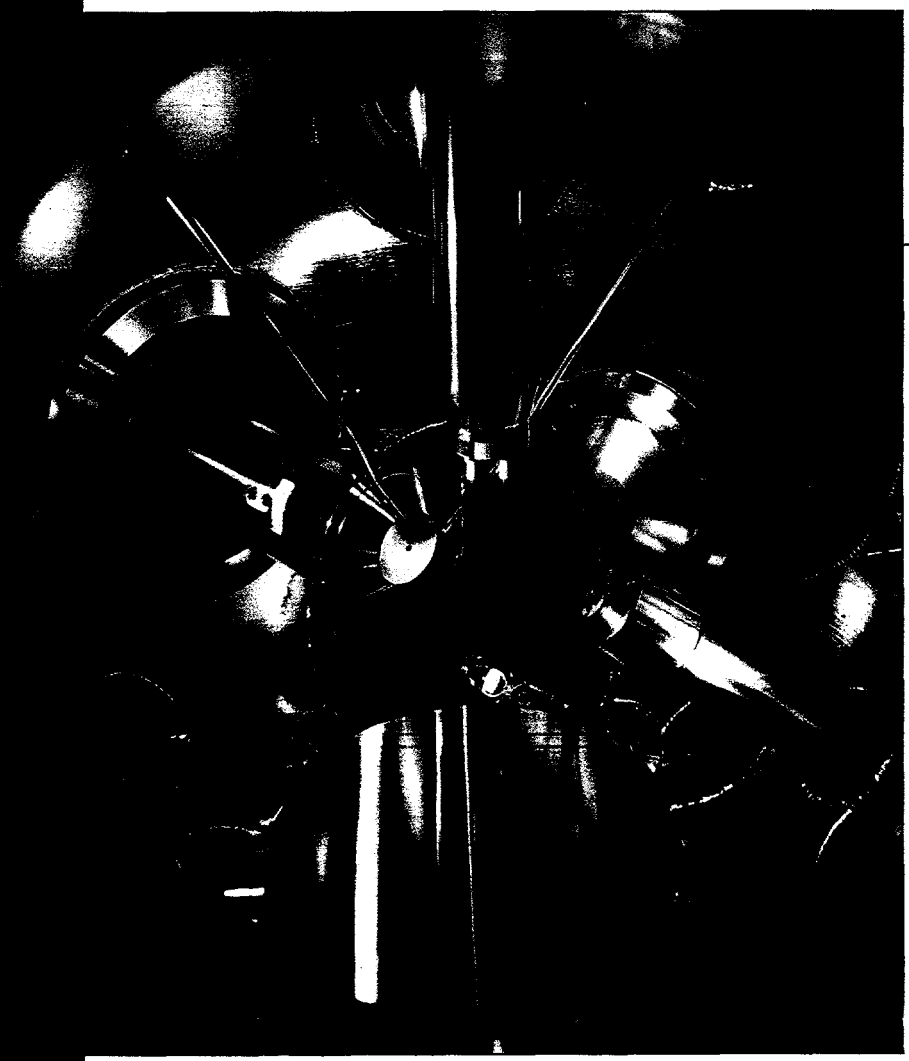
Optical Diagnostics and Laser Spectroscopy

Optical diagnostics are ideally suited to probing the hostile environment of a CVD system. They are non-intrusive, selective, sensitive, and can provide the high spatial resolution needed in the strong temperature and concentration gradients present in CVD processes. Sandia researchers have extensive experience in developing and applying such techniques to reacting flows, including CVD and combustion systems. They typically use laser Raman spectroscopy to measure gas temperatures and chemical species concentrations of starting compounds such as SiH_4, $SiCl_2H_2$, AsH_3 and WF_6. In contrast, high sensitivity approaches such as laser-induced fluorescence are available for monitoring highly reactive chemical species formed by decomposition of the reactants. This technique has been used to map spatial distributions of Si and Ga atoms, HSiCl and Si dimers in CVD processes.

The IRIS technique, which combines plasma, molecular beam, and laser technologies, allows direct measurements of radical/surface reactivities.



Ultra-high vacuum apparatus for studying the surface reactions occurring in CVD.



EXPERIMENTAL CAPABILITIES

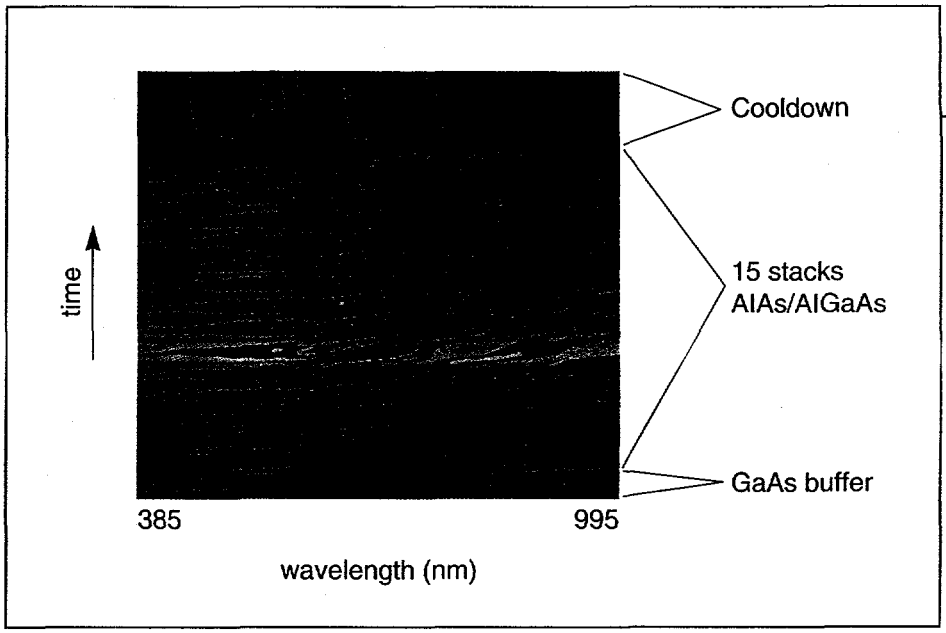
Molecular Beam Methods for Gas/Surface Reactivities

Molecular beam methods are used to measure gas/surface reaction probabilities under conditions that eliminate interference from the gas-phase reactions or transport limitations that are generally present in CVD reactors. For example, the CVD starting compounds SiH_4, Si_2H_6, SiF_4 and NH_3 have been found to react at surfaces with relatively low probability (10^{-2} to 10^{-6}). Chemical intermediate species are expected to be much more reactive at surfaces than the starting compounds. Sandia has developed a novel method, IRIS (Imaging of Radicals Interacting with Surfaces), to study radical/surface interactions using molecular beam and laser spectroscopic techniques. Studies to date on SiH, SiO and NH show a wide range of reactivity (<0.1 to >0.94).

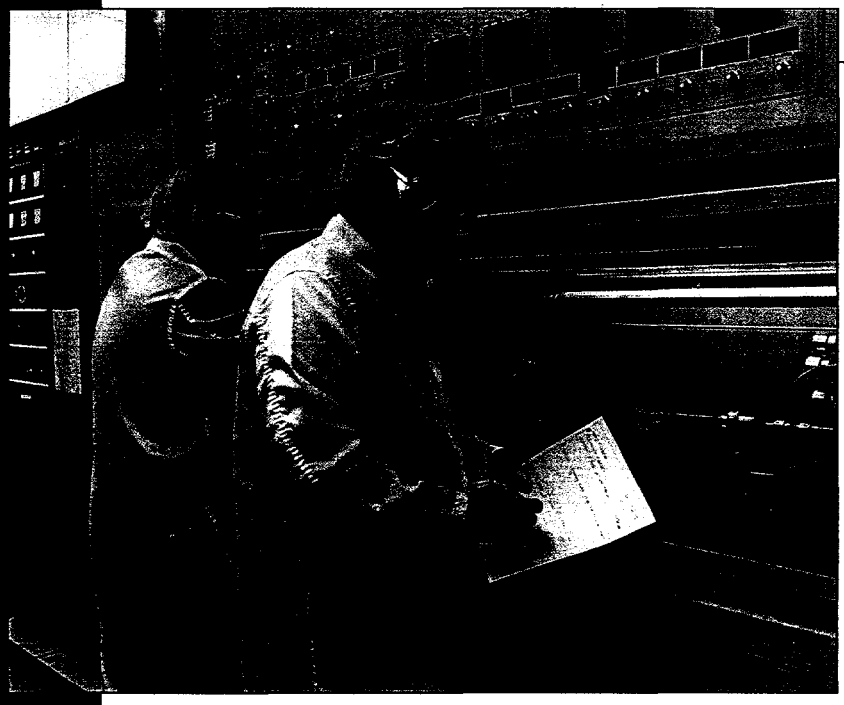
Surface Chemistry

Sandia has a complete set of modern surface-sensitive analytical techniques for elucidating mechanisms and kinetics of surface chemistry. The available techniques include LEED, Auger, XPS, static-SIMS, TPD, FTIR and molecular beam scattering. These techniques are available in multi-chambered apparati that integrate high-pressure processing chambers with UHV environments. This approach enables the isolation and study of key reactions in CVD systems. Ongoing programs are investigating the surface chemistry of GaAs deposition, the deposition of metals (tungsten, copper), and growth of insulators (SiO_2 from TEOS).

False-color image shows the use of spectroscopic reflectance as a real-time monitor during growth of GaAs/AlGaAs mirror stack.



Commercial MOCVD reactor used for growth of compound semiconductor materials and devices.



EXPERIMENTAL CAPABILITIES

Optical Process Control Sensors

CVD scientists are developing optical probes that can be used during deposition to monitor growth rates, composition and surface adsorbates. They have demonstrated that reflectance can be used as a real-time deposition rate monitor during the deposition of SiO_2 in a commercial single-wafer CVD reactor and during the deposition of a layered structure of GaAs, AlAs and AlGaAs. Additional techniques based on UV absorption have been used to monitor concentrations of starting compounds such as $Ga(CH_3)_3$, $Al(CH_3)_3$ and AsH_3 in MOCVD. Such real-time sensors can monitor the performance of bubblers and pressure control systems and can detect gas switching times.

Materials Growth and Characterization

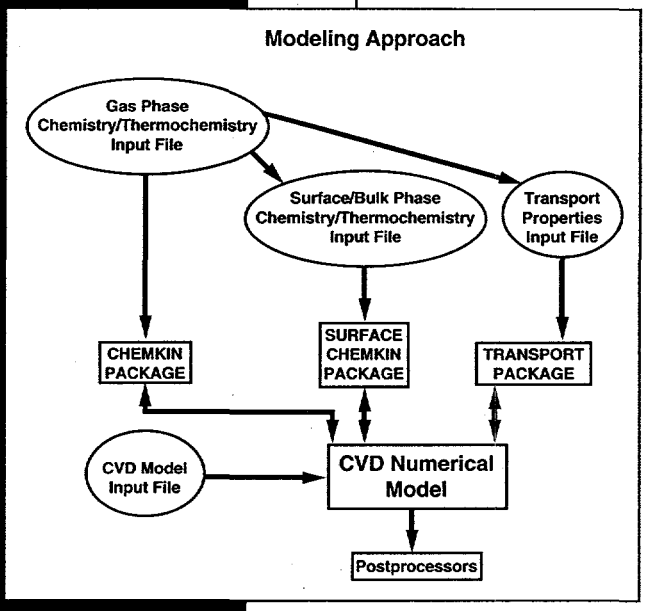
Sandia maintains state-of-the-art materials growth and characterization facilities, particularly in Metal-Organic Chemical Vapor Deposition (MOCVD). MOCVD is used for commercial production of compound semiconductors because of its ability to grow compositionally tailored and artificially structured materials (e.g. monolayer superlattices), its capacity for high through-put, and its relatively low cost. Sandia's facilities include three commercial MOCVD reactors that are used to grow device-quality epitaxial films and superlattices of aluminum, gallium and indium arsenide, phosphide and antimonide materials. The newest of these reactors, an EMCORE GS3200 Rotating Disk Reactor, is specifically targeted for the development and implementation of real-time sensors and intelligent, model-based process control. A variety of techniques are used for materials characterization, including optical microscopy, electron microscopy, (scanning or transmission), x-ray diffraction, Hall measurements and photoluminescence.

The CVD modeling software uses a modular approach.

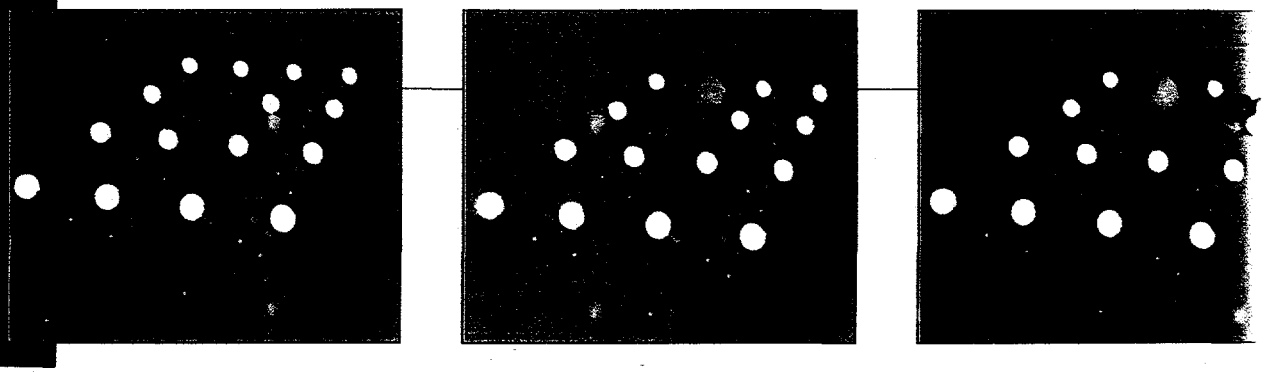
MODELING CAPABILITIES

Numerical Models

Sandia has extensive experience in the development and application of numerical models of complex reacting fluid flows. Numerical models describing gas flow in CVD reactors can be used for theoretical studies of reactor design and scale up, including details such as gas injection and mixing. The models include heat transfer, energy balances and chemical reaction mechanisms of varying degrees of complexity. Due to computational limitations, the more complex heat and mass transfer models can only be used with simple chemistries, whereas complex chemical mechanisms are generally studied with simple geometry models.



Existing CVD codes include: PSR (perfectly-stirred reactor), which describes deposition in a zero-dimensional system; SPIN, which describes deposition in one-dimensional stagnation-point flows or in rotating disk systems; CRESLAF, which describes deposition in two-dimensional systems, e.g. flow between two infinitely wide flat plates or through a cylindrical chamber; and OVEND, which describes deposition in many-wafer low pressure CVD ovens.



MODELING CAPABILITIES

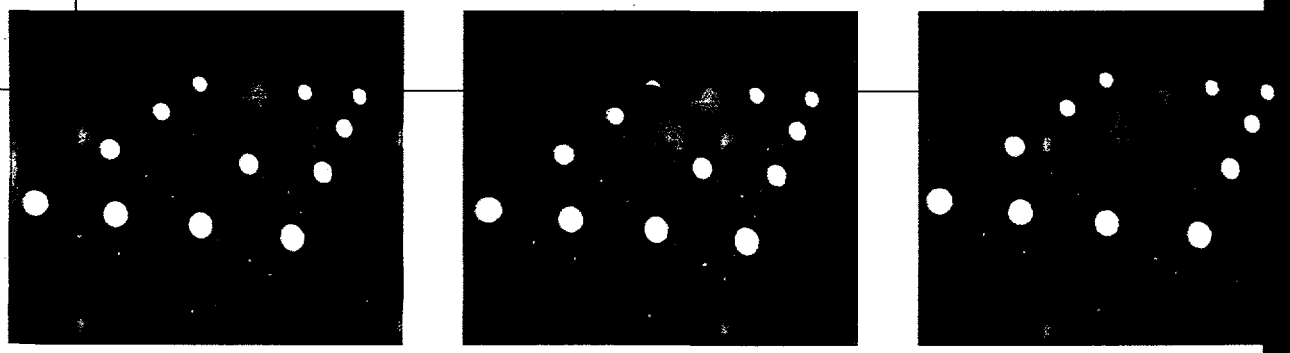
CHEMKIN and Surface-CHEMKIN

The CHEMKIN and Surface-CHEMKIN software packages allow reacting chemical systems to be modeled in a simple, easily modified manner. The user writes the mechanism in standard chemical notation with standard rate parameters. Gas-phase, gas-surface and surface reactions are easily handled, although the user must provide the reaction mechanism and the kinetic parameters.

CHEMKIN is easy to use on a variety of computer platforms.

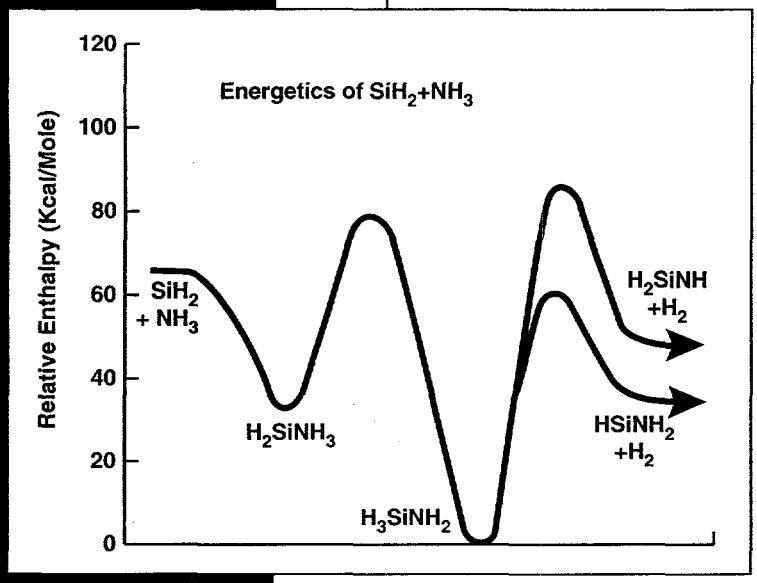
Development of Chemical Reaction Mechanisms

Chemical reaction mechanisms are needed to describe the reactions occurring both in the gas and at the surface in a CVD process. In developing these mechanisms, Sandia scientists draw on kinetic data in the literature, if available. If not, they use standard methods for estimating kinetic parameters and the underlying thermochemical parameters. The overall reaction mechanism is then refined with experimental measurements of key kinetic parameters (identified by the model) as well as deposition rate measurements from simple, well-defined research systems. To date, mechanisms of varying levels of sophistication have been developed that describe the deposition of silicon from SiH_4, GaAs from $Ga(CH_3)_3$ and AsH_3, diamond from hydrocarbons, and Si_3N_4 from SiF_4 and NH_3.



Surface reactions leading to diamond deposition.

Quantum chemistry calculations can provide the thermochemical and kinetic information, shown here for silylamine, needed to understand CVD systems.

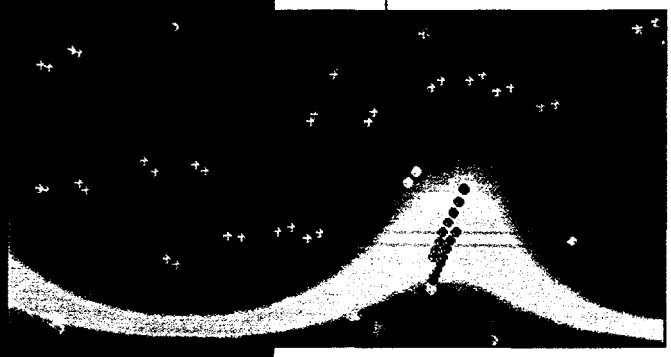


MODELING CAPABILITIES

Thermochemical and Transport Data

Sandia has databases of thermochemical and transport properties needed to model CVD. The database contains more than 300 compounds, including data from the JANAF tables. For many CVD systems, however, the literature does not contain the needed data. In such cases, standard techniques for estimating thermochemical data are used. Alternatively, for molecules composed of relatively light atoms, the data can be obtained from ab initio electronic structure calculations using the BAC-MP4 method. This method, which combines electronic structure calculations at the relatively high MP4 level with empirical corrections, has been applied to more than 2500 compounds.

Fluid mechanics calculations of gas flow in a channel show the development of transverse waves of heated gas.



Heat and Mass Transport

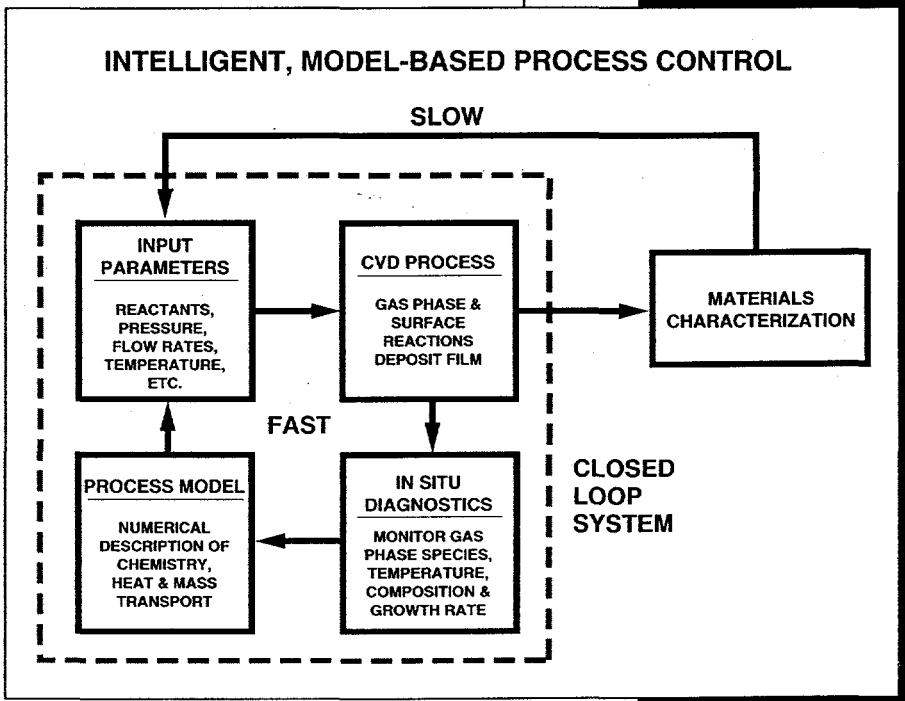
CVD depends on a complex interaction between the diffusive and convective heat and mass transport and the chemical reactions occurring in the system. Depending on the details of the reactor system, heat transport in the solid reactor walls also can influence the deposition process significantly. Sandia researchers have found that computational simulation provides a cost-effective approach to understanding and controlling the competing processes. The models are used to analyze the effects of reactor geometry (e.g., reaction-chamber shape, gas inlet manifolds, and exhaust systems) and operating conditions (e.g., gas flow rates, operating pressure, reagent composition, and reactor wall temperatures). For example, simulations can be used to find regions in parameter space that provide stable gas flows without undesirable recirculation cells.

MODELING CAPABILITIES

Model-Based Process Control

It is often difficult (or prohibitively expensive) to develop process sensors that measure film characteristics directly. As a result, CVD processes are either run "open loop" or controlled according to inferences from sensors. Physically based models are often valuable in establishing the relationship between the process sensors and the desired product properties. Developing computationally efficient models that can run in "real time" will allow such models to be incorporated directly into process-control algorithms. For example, in semiconductor fabrication, controlling the wafer temperature is often critical to the success of a CVD process. However, most CVD reactor systems cannot measure wafer temperature directly. Sandia scientists have developed physically-based models that are embedded in an advanced control architecture to control the (simulated) wafer temperature from remote thermocouple sensors.

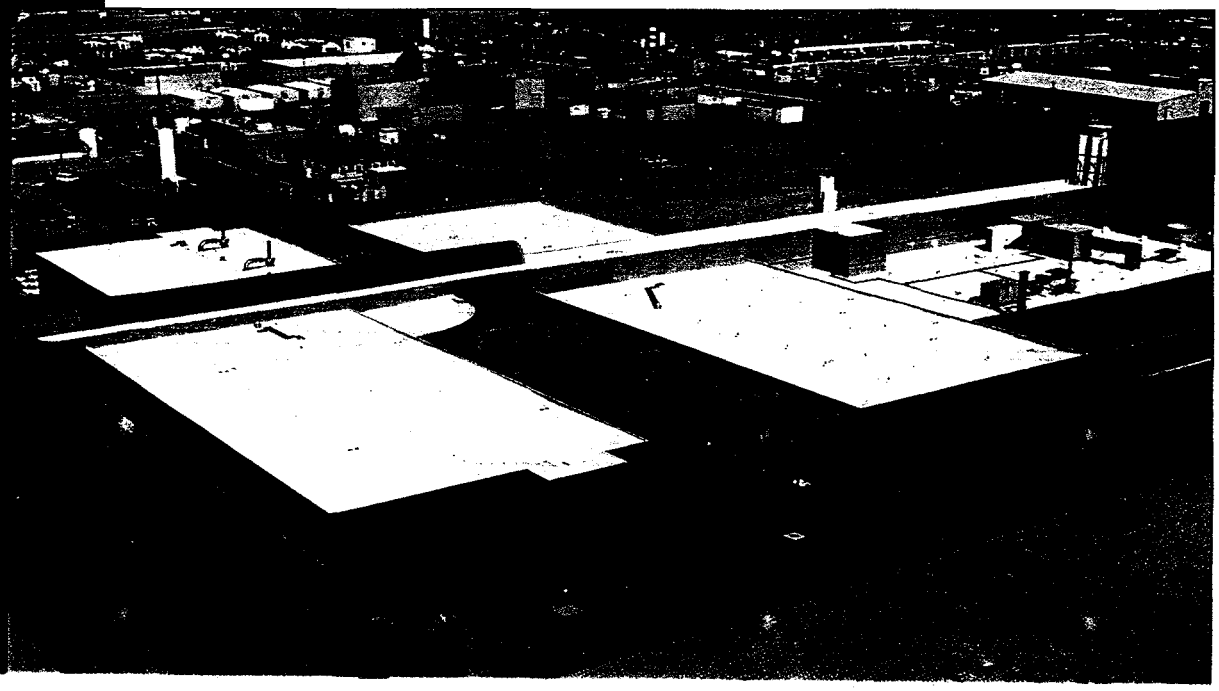
Intelligent process control combines output from in situ sensors with process models to improve CVD reactor capabilities.



RELATED FACILITIES AND LABORATORIES

CVD Sciences is a multidisciplinary and cross-organizational program. The core group is split between the Physical and Chemical Sciences Center of Sandia's Research Division in New Mexico and the Center for Materials and Applied Mechanics at Sandia, California. The program is closely coupled to other major research programs at Sandia in Materials Science, Combustion, Lasers and Optics, and Microelectronics and Photonics. Sandia's R&D activities span the range from basic physics and chemistry research to the fabrication and prototyping of silicon and compound semiconductor devices, components and systems.

Major facilities affiliated with this program include the Microelectronics Development Laboratory, with over 30,000 ft^2 of clean room space dedicated to the development of advanced microelectronic capabilities, and the Compound Semiconductor Research Laboratory, with a 4000 ft^2 clean room focused on the development, growth, and fabrication of advanced compound semiconductor devices for both microelectronic and photonic applications. Close association between the CVD scientists and the materials growth, processing and device fabrication specialists in these facilities has influenced the direction of their research towards solutions of real-world problems in manufacturing technology.



The Microelectronics Development Laboratory at Sandia National Laboratories.

PERSONNEL

Roughly 30 individuals from several organizations within Sandia National Laboratories work in CVD sciences. This includes researchers at both the New Mexico and California sites.

EXTERNAL INTERACTIONS

Collaborative efforts with industry, universities and other laboratories are encouraged at Sandia National Laboratories. For more information, contact:

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Selected Publications:

1. "A Mathematical Model of the Coupled Fluid-Mechanics and Chemical Kinetics in a Chemical Vapor Deposition Reactor," M.E. Coltrin, R.J. Kee and J.A. Miller, *J. Electrochem. Soc.*, **131**, 425 (1984).
2. "Comparisons Between a Gas-phase Model of Silane CVD and Laser Diagnostic Measurements", W.G. Breiland, M.E. Coltrin and P. Ho, *J. Appl. Phys.*, **59**, 3267 (1986).
3. "The Use of Metal Organic Chemical Vapor Deposition to Prepare Device Quality GaAsP Strained-Layer Superlattices," R.M. Biefeld, *J. Electron. Mater.*, **15**, 733 (1986).
4. "Application of Supercomputers to Modeling Fluid Transport and Chemistry in CVD Reactors," R.J. Kee, G.H. Evans, and M.E. Coltrin, Supercomputer Research in Chemistry and Chemical Engineering, *ACS Symposium Series*, 353, 334 (1987).
5. "Laser Studies of the Reactivity of SiH with the Surface of a Depositing Film", P. Ho, W.G. Breiland and R.J. Buss, *J. Chem. Phys.*, **91**, 2627 (1989).
6. "A Mechanism for Selectivity Loss During Tungsten CVD," J.R. Creighton, *J. Electrochem. Soc.*, **136**, 271 (1989).
7. "In Situ Measurement of the Metalorganic and Hydride Partial Pressures in a MOCVD Reactor Using Ultraviolet Absorption Spectroscopy," G.A. Hebner, K.P. Killeen and R.M. Biefeld, *J. Cryst. Growth*, **98**, 293 (1989).
8. "Hydrogen Chemisorption and Reaction on GaAs(100)," J.R. Creighton, *J. Vac. Sci. Tech.*, **A8**, 3984 (1990).
9. "Surface Chemkin: A General Formalism and Software for Analyzing Chemical Kinetics at a Gas-Surface Interface," M.E. Coltrin, R.J. Kee, and F.M. Rupley, *Intl. J. Chem. Kinetics*, **23**, 1111 (1991).
10. "Theoretical Study of the Thermochemistry of Molecules in the Si-N-H-F System", C.F. Melius and P. Ho, *J. Phys. Chem.*, **95**, 1410 (1991).
11. "Design and Verification of Nearly Ideal Flow and Heat Transfer in a Rotating Disk CVD Reactor," W.G. Breiland and G.H. Evans, *J. Electrochem. Soc.*, **138**, 1806 (1991).
12. "Chemisorption of Trimethylaluminum and Ammonia on Silica: Mechanisms for the Formation of Al-N Bonds and the Elimination of Methyl Groups Bonded to Aluminum," M.E. Bartram, T.A. Michalske, J.W. Rogers, Jr. and T.M. Mayer, *Chemistry of Materials*, **3**, 953 (1991).
13. "Improving the Performance of $InAs_{1-x}Sb_x$/InSb Infrared Detectors Grown by Metalorganic Chemical Vapor Deposition," R.M. Biefeld, J.R. Wendt, and S.R. Kurtz, *J. Cryst. Growth*, **107**, 836 (1991).
14. "Unsteady Three-Dimensional Mixed Convection in a Heated Horizontal Channel with Application to Chemical Vapor Deposition," G.H. Evans and R. Greif, *Intl. J. Heat Mass Transfer*, **34**, 2039 (1991).
15. "The Growth of InSb Using Alternate Organometallic Sb Sources," R.M. Biefeld, *J. Cryst. Growth*, **128**, 511 (1993).
16. "A Thermal Desorption Investigation of Arsine Chemisorption on Ga-Rich and As-Rich GaAs(100)," B.A. Banse and J.R. Creighton, *Surface Science*, **278**, 317 (1992).
17. "Reactive Chemical Intermediates in Metal-organic Chemical Vapor Deposition of GaAs," K.P. Killeen, *Appl. Phys. Lett.*, **61**, 1864 (1992).

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