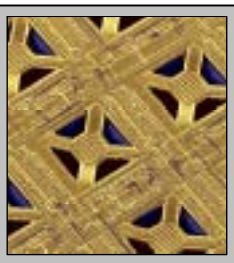
I. Process Measurements Division
James R. Whetstone, Chief

A. Division Overview

Mission:

The Process Measurements Division establishes and disseminates national measurement standards for thermodynamic parameters and engages in research in measurement science to improve measurement capabilities for chemical process and related technologies. Research efforts seek to enhance U.S. national measurement standards, their realization and dissemination, measurement techniques, recommended practices, sensing technology, instrumentation, and mathematical models required for analysis, control, and optimization of industrial processes. The Division is responsible for national measurement standards for temperature, humidity, pressure and vacuum, fluid flow, air speed, liquid density and volume. Its research efforts seek fundamental understanding of, and generate key data pertinent to, chemical process technologies. These efforts include the development and validation of data-predictive computational tools and correlations, computer simulations of processing operations, and provision of requisite chemical, physical, physical property, and engineering data.



Process Measurements

J. Whetstone, Chief

- Fluid Flow
- Process Sensing
- Thermometry
- Pressure & Vacuum
- Thermal & Reactive Processes
- Fluid Science

Organizational and Project Structure:

The Division has 67 full and part-time staff members, organized in 6 groups, representing a range of technical competencies and is organized to establish, strengthen and extend them. Additionally the Division has 41 guest researchers working with our staff on various project activities. Competencies, research efforts, and standards activities are focused in the 12 project areas shown at the right. The 2-digit Process Measurements Division group number or the 3-digit (italicized) NIST Division number given in square brackets in the project listing indicates group or Division responsibilities for each project. In several cases competencies required for successful accomplishment of project objectives cross Group and/or Division organizational lines.

In 2004 project responsibilities for the Thermal and Reacting Processes Group were changed to include the Molecular Electronics project as well as refocusing our efforts in both gas and particulate concentration standards and measurements into a new project named Gas and Particulate Concentration Standards and Measurements. Staff working in these areas and previously assigned to Division Office, the Thermometry Group, and the Analytical Chemistry Division were reassigned to the Thermal and Reacting Flows group.

Process Measurements Division Projects

- Flow Measurements and Standards [01, 06]
- Temperature Measurements and Standards [05, 08]
- Pressure and Vacuum Measurements and Standards [06]
- Humidity Measurements and Standards [05]
- Microfluidics and BioMEMS [04, *839*]
- Chemical Sensing with Micro-Arrays [04]
- Molecular Electronics [00, *837, 812*]
- Plasma Process Metrology [04]
- Advanced IC Interconnects – Process Metrology and Models [07]
- Optoelectronics [07, *837, 839*]
- Acoustic Measurements and Methods for Thermophysical Properties [08]
- Gas and Particulate Concentration Standards and Measurements [07, *837*]

Fluid Flow Group – 836.01

- Flow rate measurements;
- Computational fluid dynamics;
- High accuracy liquid volume and density measurements and standards; and
- Anemometry.

Primary responsibility for the Flow Measurements and Standards project.

Process Sensing Group – 836.04

- Plasma processes, models, radio frequency and optical diagnostic and measurement methods;
- MEMS-based gas sensor arrays, deposition of gas sensitive thin films, and operation and testing of gas sensors;
- Mono-molecular self-assembly chemistries;
- DNA probe/target sensing approaches; and
- Molecular recognition strategies.
- Physical and chemical measurements in micro-fluidic devices.

Primary responsibilities for the Plasma Process Metrology, Chemical Sensing with Micro-Arrays, and Micro-Fluidics and Bio-MEMS projects.

Thermometry Group – 836.05

- Development and operation of fixed-point cells defining temperature scales;
- Primary acoustic thermometry;
- Resistance thermometry;
- Cryogenics and low temperature thermometry;
- Thermodynamic methods for the generation of moisture in gases – humidity measurements; and
- Cavity ring-down spectroscopy - gas and liquid.

Primary responsibilities for the Temperature and Humidity Measurements and Standards projects.

Pressure and Vacuum Group - 836.06

- Primary manometry;
- All aspects of vacuum gauging;
- Very low gas flow rate measurements and standards;
- Piston gauge characterization and calibration; and
- Pressure gauging of all types.

Primary responsibility for the Pressure and Vacuum Measurements and Standards project.

Thermal and Reactive Processes Group – 836.07

- Two Photon Photoelectron Spectroscopy
- Molecular Self Assembly
- Raman Spectroscopy;
- Optical diagnostic techniques;
- Aerosol transport and diagnostic measurements;
- Computational fluid dynamics;
- Chemical vapor deposition reactor modeling;
- Combustion processes; and
- Liquid atomization.

Primary responsibilities for the Advanced IC Interconnects – Process Metrology and Models, Molecular Electronics, Optoelectronics, and Gas and Particulate Standards and Measurements projects.

Fluid Science Group – 836.08

- Measurements of thermophysical and properties of fluids and fluid mixtures;
- Statistical Physics;
- Equations of State;
- Acoustic measurement techniques; and
- High accuracy capacitance measurements;

Primary responsibility for the Acoustic Measurements and Methods for the Thermophysical Properties project. Contributes to the Pressure and Vacuum, Temperature and Flow Rate Measurements and Standards projects.

Program Areas:

Our measurement science research and standards realization and dissemination activities are found in 9 of CSTL's 14 program areas. These are:

- Automotive and Aerospace
- Data and Informatics
- Energy Systems
- Forensics and Homeland Security
- Health and Medical Products and Services
- Industrial and Analytical Instruments and Services
- International Measurements and Standards
- Microelectronics
- Technologies for Future Measurements and Standards

The Division has responsibilities for establishing, enhancing, and disseminating national measurement standards; summarized in the first four project descriptions given below. Dissemination of these standards via a broad competency in instrument calibration processes and procedures is a strong contributor to meeting these responsibilities. These efforts provide traceability of measuring instruments for U.S. industry and government agencies. We utilize Standard Reference Materials and Data

where thse more effectively provide traceability to U.S. national measurement standards.

Demonstration the level of equivalence of U.S. national measurement standards with those of other nations has been a significant effort for a number of years and have focused on key comparison activities organized by the consultative committees of the Comité International des Poid et Mesures (CIPM) and by Regional Metrology Organizations. NIST is a leading member of the Sistema Interamericano Metrologia (SIM – the Inter-American Metrology System), the RMO of the Americas. Over the past several years, a substantial number of comparisons have been completed in temperature, pressure and vacuum standards. Few needs remain in these areas at the CIPM level for the next few years. New efforts at a reduced scale are in the planning stage in the SIM organization. The Working Group on Fluid Flow of the Consultative Committee on Mass is mounting several CIPM key comparison efforts having NIST involvement, either as a participant or for organizing and executing responsibilities of the pilot laboratory for a Key Comparison.

Project Efforts

Temperature Measurements and Standards

NIST was the first NMI to fully realize the ITS-90 for contact thermometry in the range of 0.65 K to 1235 K. The Process Measurements Division effectively disseminates the ITS-90 to a broad range of users. Research efforts focus on advancing the state-of-the-art in thermometry by developing methods and devices that enable this broad user community to attain traceability to the ITS-90 in demanding industrial environments. Furthermore, this project:

- Assists user groups in the assessment and enhancement of the accuracy of their temperature measurements,
- Promotes effective measurement methods through participation in standards development organizations,
- Measures the deviations of the ITS-90 from thermodynamic temperature values as a basis for future improvement of temperature scales, and
- Improves temperature measurements and standards and methods of their dissemination.

Flow Measurement and Standards

National measurement standards for fluid flow rate and related quantities are developed and disseminated through the following calibration services:

- Gas flow rate – 0.04 to 77,600 slm;
- Water flow rate – 8 to 38,140 slm;
- Liquid hydrocarbon flow rate – 0.04 to 1,140 slm;
- Liquid volume – 3.8 to 7,600 L;
- Liquid density – 600 - 2000 kg/m^3;
- Air speed in the range of 0.2 to 75 m/s.

Research efforts advance the state-of-the-art in flow measurements through the development of measurement standards that minimize measurement uncertainty and improve the quality of fluid measurements for the custody transfer of fluids in commerce. The Fluid Flow Group's efforts establish levels of comparability among National Metrology Institutes (NMIs) and strengthen measurement traceability procedures of U.S. national standards for flow rate measurement.

Humidity Measurements and Standards

NIST realizes humidity standards based on thermodynamic generation and disseminates through calibration services. Research efforts and standards activities focus on:

- Expanding the range of humidity standards;
- Developing and enhancing primary humidity measurement standards;
- Demonstrating levels of equivalence of U.S. national measurement standards with those of other nations; and
- Engaging in education and outreach efforts to improve industrial hygrometry practices.

Water vapor is a primary contaminant in process gases required by many industrial processes. Integrated circuit manufacturing requires very low moisture (μg/g) and trace (ng/g and pg/g) levels. The Division continues to extend the range of its standards, pushing capabilities to generate moist gases into the picogram/gram region in the coming year using thermodynamic generation methods.

Pressure and Vacuum Measurements and Standards

Pressure and vacuum measurements are used in industrial, aerospace, and transportation applications to achieve manufacturing quality, throughput, and performance. In many cases pressure and vacuum measurements are important to public health and safety. The efforts of this project:

- Provides national measurement standards for pressure and vacuum, (from 10^{-7} to 10^{+8} Pa) and low gas flowrate (10^{-13} to 10^{-3} mol/s) through the provision of measurement services available to industry, government, and the public;

- Develops improved measurement standards and techniques for pressure, vacuum, and low range flow measurement;
- Demonstrates levels of equivalence of U.S. national measurement standards with those of other nations.

Efforts in FY 2004 were focused on moving this project to the new Advanced Measurements Laboratory (AML). These activities will include improvements to various standards. Their operation in the much improved environment of the AML is anticipated to improve NIST's capabilities in this area in the future.

Chemical Sensing with Micro-Arrays

Real-time sensing of gas phase chemical species has application areas as diverse as automotive exhaust gas speciation to detection of chemical warfare agents. Chemical micro-sensor arrays are based on NIST-developed, and patented, 'micro-hotplate' (μHP) arrays formed by silicon micro-machining and similar devices such as differential-scanning calorimeters. Chemical sensors are fabricated by depositing metal oxides, e.g., SnO_2, and surface-dispersed catalytic metal-additives on the micro-hotplate to form robust, electrical-conductance-based sensing elements capable of detecting a range of organic species. Both species identification and quantification have been demonstrated with individual devices and arrays. Methods have been developed and demonstrated that significantly increase the sensitivity and stability of micro-hotplate chemical sensors. Sensitivity to organic analytes, e.g., methanol in air at the 10 ng/g level, has been demonstrated as has sensitivity to similar levels toxic industrial compounds and chemical warfare simulants and agents. Detection at these levels in the presence of interfering compounds with 1,000 to 100,000 times the concentration has been a primary research effort in FY 2004 and has resulted in advances in the capabilities of this technology. Efforts to improve sensitivity of sensing films using nano-phase materials has also enjoyed some success. These efforts are described in on of the technical articles below. catalyst-doped films.

Micro-Fluidics and Bio-MEMS

Micro-fluidic and Bio-MEMS device technologies promise to accelerate the merging of biological systems with micro-machined technology to develop selective, miniaturized chemical and biochemical measurement tools incorporating molecular recognition and related technologies. Research efforts seek to develop metrology methods and tools to characterize the performance of micro-fluidic devices and structures. Such new tools hold vices and structures. Such new tools hold tremendous promise for point-of-care health care measurements and for rapid detection of potential bio-terrorism pathogens. Major scientific and technical challenges to be overcome include:

- Developing robust, self-assembly-based protocols, with sub-micrometer resolution, for directing and attaching biological molecules to MEMS structures;
- Developing analytical techniques for characterizing the activity of biological/MEMS structures;
- Ensuring compatibility of MEMS devices with aqueous biological environments; and
- Developing novel MEMS-based transduction strategies for detecting biological recognition events.

Advanced IC Interconnects – Process Metrology and Models

To achieve higher operating frequencies, semiconductor devices of the future will be fabricated with on-chip interconnections (wiring) consisting of thin films having (1) dielectric constant values lower than that of currently used silicon dioxide and (2) a thickness significantly below that of those currently used. In addition, copper will replace aluminum as the interconnection metal. Low dielectric constant (Lo K) films are composed of a number of materials systems most of which are porous. Copper readily diffuses through the currently used SiO_2 films necessitating the use of very thin diffusion barrier layers placed between the copper bulk conductor and the dielectric, SiO_2. Use of Lo K insulating films will also require diffusion barrier layers effective on surfaces of varying porosities and with thickness of 10 nm and below for feature sizes in the sub-100 nm region. A variety of metrology needs are associated with the use of Lo K materials at sub-100 nm features dimensions. Although recent advances in the electrochemical deposition processes currently used for copper deposition are anticipated to meet deposition needs below 100 nm feature sizes, these require a seed layer to operate effectively. The currently used physical vapor deposition of seed layers is not useful for sub-100 nm where aspect ratios of 10:1 are planned. Chemical vapor deposition of copper is the process that has been identified as the best candidate for seed layer deposition. The International Technology Roadmap for Semiconductors – 2000 Update has a "No Known Solution" entry for many of the process modeling and simulation requirements necessary to support development and copper CVD for interconnect seed layers and fills is

identified as an area requiring research. Research efforts address the need for the development of fundamental reaction mechanisms and rate constants (both gas/plasma and surface) that are key to properly capturing the physics and chemistry of surface evolution during thin film deposition. Research efforts seek to:

- Develop models of thermal decomposition models for deposition of both diffusion barrier and metal layers in Lo-k materials;
- Develop and validate 1 and 2 dimensional reactor models that include particle formation, agglomeration, transport, fluid dynamic and thermophoretic effects;
- Develop process metrologies supporting deposition of copper seed layers; and
- Investigate atomic layer deposition methods as an alternative to chemical vapor deposition for ultra-thin barrier layers.

Optoelectronics

Free carrier transport is central to the operation of all optoelectronic devices. Measurement of free carrier concentration and mobility is critical in determining the material quality. Current practice utilizes Hall Effect or capacitance probe methods that require electrical contact to metal probes. If available, non-contacting methods would allow in-situ and ex-situ measurement and inspection. A spatially resolved method would also provide the means improve process uniformity and control. Raman spectroscopic methods do not require physical contact with the material in addition to having excellent sensitivity to interaction between free carriers and polar lattice vibrations. From the Raman spectrum, the majority carrier properties are determined by fitting of appropriate spectral models.

Research efforts seek to:

- Develop in situ, non-destructive probes of III-V semiconductor carrier properties suitable for spatially resolved measurement and process monitoring and control during film growth and etch processing;
- Incorporate temperature dependence on materials properties, i.e., band structure, carrier concentration, and carrier effective mass to allow measurements at growth temperatures; and
- Develop a spectral simulation model for quantitative determination of carrier concentration and mobility from Raman spectra.

Plasma Process Metrology

Some of the most important processes in semiconductor manufacturing are plasma processes used to deposit and etch the thin films that form integrated circuit devices. Plasma processing reactors have historically been designed and operated using empirical methods alone, but continued evolution of these manufacturing tools requires a much greater reliance on process and reactor modeling. Indeed, model-based process design and control are important needs identified in the *International Technology Roadmap for Semiconductors*. To obtain more reliable predictions of the spatial uniformity, chemistry, and electrical properties of processing plasmas, further progress in model development and validation is required. Also, to enable improvements in process control, a need exists to develop sensors that are compatible with the manufacturing environment. Experimental efforts use reference reactors as test beds for validating models and testing new measurement techniques. These reactors provide a well-defined basis for comparison of measurements between laboratories and are equipped with a wide variety of plasma diagnostic tools that measure the chemical, physical, and electrical properties of plasmas. Information provided by the set of diagnostics allows testing of models. Also, sensors designed for manufacturing environments can be tested and compared with diagnostic results. These efforts are combined with complementary tasks undertaken by EEEL and PL.

Research efforts seek to:

- Develop advanced chemical and electrical measurement methods, diagnostic techniques, and models to characterize plasma etching and deposition processes to enhance continued progress in process optimization, process control, and model-based reactor design;
- Develop rf electrical measurement techniques for the accurate determination of electrical parameters in rf plasma reactors supporting comparison of reactor performance and operating conditions and set points; and
- Develop plasma sheath models for use with rf electrical measurements to non-intrusively determine ion flux and energies at the wafer surface. Utilize these developments as the basis for new approaches to non-invasive measurement of plasma parameters.

Molecular Electronics

As silicon-based electronics components approach inherent performance limits, small molecular ensembles are seen as the active elements are seen as a viable, next-generation technology. NIST is developing measurement methods, standards, and data that are critical to the realization of molecular elec-

tronic components. This project is collaborative with Divisions 837, 838, and EEEL.

Research efforts seek to develop:

- Test structures supporting characterization of the electrical properties of ensembles of molecules;
- Methods and procedures to evaluate current-voltage transport in molecular systems;
- Models of electronic structure/transport mechanisms in molecular electronic systems; and
- Computational models of conducting molecules.

Acoustic Measurements and Methods for Thermophysical Properties of Gases

The thermophysical and transport properties of gases are important in a broad range of industrial processes ranging from thermo-acoustic machine design to flow rate measurement. The Division investigates fundamental physical acoustics and develops versatile and rugged acoustic resonator methods to produce accurate measurements of the speed-of-sound and viscosity of gases.

A modified Greenspan acoustic resonator with specialized transducers is being developed to measure the bulk viscosity of xenon near its critical point in earth's gravity and, eventually, in micro-gravity. These measurements will be made closer to the critical point than ever before and may resolve long-standing discrepancies between theory and experiment. This work exploits expertise gained from the previous measurements of the shear viscosity of near-critical xenon in micro-gravity.

Mass flow controllers (MFCs) are ubiquitous for gas delivery to process chambers used in integrated circuit manufacturing. Individual process tools use 20 - 50 MFCs often operating in the flow rate range 1 to 1000 sccm. Continued increases in process reproducibility requirements drive improvements in MFC accuracy and stability. Thermophysical property data are used to calculate gas conversion factors that predict MFC flow performance with reactive process gases from calibration data obtained with non-reactive gases. NIST research will improve standards in this low flow rate range and thermophysical property data for chemically reactive process gases with efforts to:

- Measure the equation of state and transport properties of the gases used in semiconductor processing with the uncertainties required by industry;
- Develop computational tools for evaluating, correlating, and (where possible) predicting these properties, and
- Disseminate property data via a user-friendly database and archival publications. As data are acquired, they are posted at http://properties.nist.gov/fluidsci/semiprop/. The properties are: speed-of-sound, heat capacity, density (equation of state), viscosity, and thermal conductivity.

Gas and Particulate Concentration Measurements and Standards

Research efforts focus on the development and aggregation of core metrologies necessary to provide (1) reference line intensity data for spectroscopic gas concentration standards and (2) reliable measurements of the physical and chemical properties of the particulate matter found in the atmosphere.

The realization of intrinsic standards for gas concentration measurement will be based upon high-precision measurements of optical absorption line intensities. Methods and/or mechanisms will be established for disseminating accurate spectroscopically-based number density measurement to NIST customers through the fundamental characterization of next-generation commercial optical spectrometers. To link current standards with these will require their comparison with existing NIST primary standards.

To improve the understanding of airborne particulate matter (PM) and its effects upon human health a major coordinated effort across Federal and State agencies is underway. An essential element in advancing the atmospheric science of fine particles is the ability to make reliable measurements of the physical and chemical properties of the particulate matter. Significant uncertainty exists regarding the quality of the measurements, and how well the data sets represent the actual PM source signatures. Several NIST Divisions will develop metrologies and PM reference materials for calibrating analytical instrumentation that discriminate and quantify PM-carbon into elemental, organic, and inorganic fractions. Three types of materials are necessary to allow measurement traceability to standards and improve inter-laboratory reproducibility, pedigreed PM (i.e., non-complex PM with clear traceability to the SI), simulated PM (i.e., blended mixtures of non-complex PM materials to resemble real PM), and real PM (serving as measurement benchmarks). Research efforts seek to develop:

- A suite of reproducible carbon-based PM reference materials with properties closely approximating that of natural PM;

- A benchmark data set to correlate liquid-phase fuels and combustion characteristics with PM morphology and thermo-optical properties; and
- Provide data for droplet-laden, homogeneous turbulent flow around obstacles for validation of fire suppression models.

Division Contributions to CSTL Programs:

The Division research efforts and standards activities contribute to the CSTL programs listed above.

Brief descriptions and summaries of some FY 2003 accomplishments follow. More detailed descriptions of these accomplishments are given in the technical articles that follow this overview.

Industrial and Analytical Instruments and Services Program

The instrumentation manufacturing industry is an important customer for NIST, providing a broad interface between users of measuring instrument and the national measurement standards realized and disseminated by NIST. Activities in the four standards-oriented projects of the Division, i.e., Measurements and Standards for Fluid Flow, Temperature, Pressure and Vacuum, and Humidity focus on both standards realization and dissemination. Division Staff interact with a wide variety of instrumentation manufacturers who rely on our measurement services to provide traceability to U.S. national measurement standards.

Calibration Services

Instrument calibration services are the primary method used by the Division for dissemination purposes. The chart in Figure 1 summarizes the level of activity in the major calibration service areas offered over the period 2001 thru 2004. Some services see significant fluctuation caused by demand variability, due to both internal and external drivers.

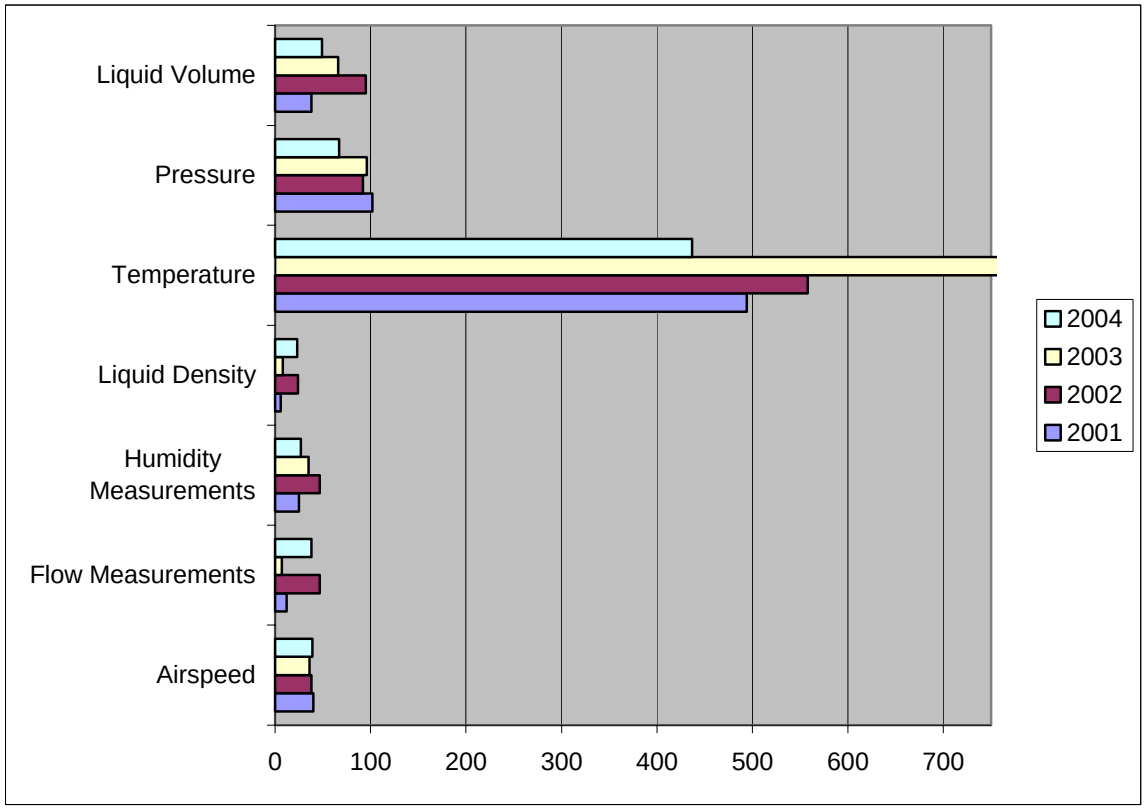


Fig. 1. Process Measurements Division Instrument Calibrations for Fiscal Years 2001 through 2004

The total calibration workload across the Division was 680 test folders. This was a significant decrease from the previous year, primarily due to the decrease in thermometry calibrations. In FY 03 the Division successfully addressed the needs of the new Advance Measurements Laboratory building for high accuracy thermistors as part of the building's HVAC system. The Thermometry Group calibrated the thermistors used in the AML laboratories requiring temperature control at the 0.1 ºC and 0.01 ºC. This effort significantly increased our activities during FY 03 and near the beginning of FY 04. These efforts materially contributed to the achievement of these levels of control resulting in this unique level of temperature control in laboratory spaces.

Improved Realization of Measurement Standards

Research efforts associated with our standards activities seek to improve realizations of national primary standards. Accomplishments in FY04 continue to advance the Division capability to advanced approaches to standards realizations. In particular two NIST competence project were completed in FY 04, Intrinsic Pressure Standards and Johnson Noise Thermometry. In both cases the feasibility of the approaches have been demonstrated such that continuation of the research efforts are clearly warranted. Technical articles on both are included below.

International Measurement Standards

NIST is the U.S. National Metrology Institute (NMI) and the agency of the U.S. Government responsible for U.S. efforts under the Treaty of the Metre. The Committee International des Poids et Mesures (CIPM), and its various consultative committees, organizes comparison of national measurement standards. In addition, coordination of similar efforts within the Regional Metrology Organization of the America (Sistema InterAmericano Metrologia - SIM) is an important activity to extend comparison efforts to as many participants as practicable. participants as practicable.

In October 1999, NIST signed the CIPM Mutual Recognition Arrangement (MRA). The objectives of the MRA are:

- To establish the degree of equivalence of national measurement standards maintained by NMIs;
- To provide for the mutual recognition of calibration and measurement certificates (CMCs) issued by NMIs; and
- Thereby to provide governments and other parties with a secure technical foundation for the wider agreements related to international trade, commerce and regulatory affairs.

Within the framework of CIPM MRA activities, the Division has systematically compared U.S. national measurement standards to establish degrees of equivalence of U.S. national measurement standard with those of other NMIs to support the CMC capabilities reflected by our calibration services in the BIPM database of CMC claims.

http://kcdb.bipm.fr/appendixC/default.asp

The majority of these efforts have been completed. Several are in progress to support those CMCs that as yet do not have key comparison results available to support them. These international activities add value to NIST calibration services, particularly for our customers involved in international trade. These MRA-related activities are intended to guarantee recognition of U.S. standards by U.S. trading partners.

G. E. Mattingly has been the chair the CCM's Working Group for Fluid Flow (WGFF) since its inception. Upon his retirement from NIST this year, Dr. Mattingly also resigned as WGFF chair. Appointment of a new chair awaits the action of the CCM. Through FY 04 the WGFF has continued to progress in the seven flow measurement areas it defined for activities: water, hydrocarbon liquids, low-pressure air, high-pressure and high-flow natural gas, high pressure nitrogen or air, air speed, and liquid volume. NIST is the pilot laboratory for the KC on the low-pressure gas flow. Good progress have been made this year in selecting the transfer standard to be used and in characterizing it response. The comparison phase of this effort are scheduled to begin in mid-FY 05.

Quality System Supporting Calibration Services

In FY 2003 NIST established its policy on quality systems in support of measurement services. This policy supports self-declaration of quality systems supporting

The NIST-level quality manual has adopted for use and conforms to the requirements of ISO 17025 with minor modifications deem appropriate to a National Measurement Institute such as NIST. Each NIST Laboratory/Division disseminating measurement standards responsibilities is required to have a fully documented quality system in place. The approach is uniform across NIST, multi-tiered and modular and has the objective of being independent

and objective while being self-assessed. It is focused on quality management as opposed to technical competence, which is presumed.

Full operation of the NIST Quality System has had two primary phases:

- Completion of initial documentation assessments by December 31, 2003 and
- Completion of full assessments by December 31, 2004The Process Measurements Division

completed the initial documentation assessment of its quality system in FY03. In FY 04 the documentation was changed to be compliant with ISO 17025 in preparation for and assessment by NIST. Assessment by a NIST assessor team was completed in September 2004. This assessor team was drawn from NIST staff members trained in quality system assessment procedures who are staff members of other NIST Divisions and/or Laboratories having standards responsibilities, and staff from the NIST Voluntary Laboratory Accreditation Program. All Division Staff directly involved in calibration and standards realizations participated in the audit. As a consequence, the Division's quality system has been presented to the SIM organization for acceptance as the final step toward acceptance of Division-provided NIST CMCs. SIM has accepted the adequacy of our quality system for the support of our CMC claims.

Microelectronics

The NIST National Semiconductor Metrology Program (NSMP) is managed by the Office of Microelectronic Programs (OMP) of the NIST Electronics and Electrical Engineering Laboratory. CSTL competencies in several areas contribute to metrology developments needed in semiconductor manufacturing. Working with the OMP, the Division selects, develops, evaluates, and validates process measurement technologies important in semiconductor manufacturing. Several projects support advances in semiconductor metrology focused on specific manufacturing technologies where metrology issues must be resolved to realize goals set by the industry. Division research and development efforts include:

- Measurement tools for molecular electronic devices;
- Thermometry techniques for characterization of thermal systems used in critical manufacturing processes and the calibration of on-line measurements in thermal processing equipment, e.g, radiometers used to control rapid thermal processing (RTP) systems;
- Standards and physical property data for reactive gases to improve mass flow controller performance;
- Measurements and models of atomic layer deposition processes anticipated for use in future generation manufacturing;
- Methods to determine electrical, physical, and chemical properties of plasmas used for etching and reaction chamber cleaning processes; and
- Water vapor measurements and standards at the nanogram/gram level for contamination control in process gases.

In some cases, we make use of processing reactors prototypical of industrial manufacturing. This allows critical tests of the measurement approach and its utility for the intended application. These complex systems strongly coupled chemistry with mass-transport and, in the case of plasma reactors, complex electrical interactions. We develop reference reactors that allow us to effectively model chemical and physical mechanisms controlling reactor operation and to validate these as part of our measurement support activity. These models and supporting data play a critical role in the Semiconductor Industry Association's (SIA) ITRS. In fact, modeling is specifically identified not only as a "crosscutting technology," but also as "pervading all crosscuts." Our program in this area, partially supported by NIST's National Semiconductor Metrology Program, seeks to develop and validate benchmark chemical mechanisms and supporting thermochemical and kinetic data, for equipment and process design and control.

Data and Informatics

Division efforts supporting this CSTL program result from activities in the Particulate Measurements and Standards projects where data involving the new generation of non-ozone-depleting Halon alternative fire retardants were completed in FY 03 to validate CFD models being developed for fire suppression applications. An accurate representation of droplet transport is crucial to understanding the physics of droplet transport around and behind solid objects. The final results have been obtained using particle image velocimetry, phase Doppler interferometry, and visualization techniques. A description of this work is given in the technical reports following this overview.

Energy Systems

The Fluid Flow Group recently complete the testing phase of an effort to demonstrate the level of equivalence of natural gas flow metering laboratories in North America. Custody transfer of natural

gas utilizes metering stations in pipelines ranging in diameter from ~100 mm to ~1 meters. NIST worked closely with the Gas Technology Institute, the American Gas Association, and the Colorado Engineering Experiment Station, Inc. (CEESI) to develop and demonstrate testing protocols and a transfer standard to compare laboratory performance. Our three partners in this effort were CEESI, Southwest Research Institute, and Trans Canada Calibrations, Inc. These institutions calibrate most metering devices used in pipeline metering stations for custody transfer operations in North America. Working with the NIST Statistical Engineering Division, the protocols and experimental design were developed and implemented. Data analysis was completed and the draft final report reviewed by the participants. This will be completed in the 1st quarter of FY 05.

Technologies for Future Measurement and Standards

Research efforts in two Division projects primarily contribute to this CSTL program, the Chemical Sensing with Micro-Arrays and Micro-Fluidics and Bio-MEMS projects. The Chemical Sensor project investigates advanced approaches to real-time sensing and measurement of gas phase chemical species based on solid-state chemical sensing arrays. New methods and techniques are also investigated supporting new transduction strategies for measurement of gas phase, chemical species. Building on prior year efforts nanowires and carbon nanotube growth on prototype sensing structures has been achieved.

Forensics and Homeland Security

An application of the NIST-developed Chemical Sensing With Micro-Arrays project is the use of this approach to the detection of chemical warfare and related materials. In FY 04 significant progress was made in demonstrating their capabilities for both compound identification and detection. Response testing with both simulants and agents in the presence of high concentrations of interfering compounds has been conducted. The results of these tests address demonstration of the potential of this technology to support monitoring and first-responders utilization. Additional information on these results in given in an article given below.

Health and Medical Products and Services

Extensive application of micro-fluidic devices to health related diagnostic products are anticipated. Incorporation of micro-scale detection will facilitate the use of these systems. This project addresses one of the outstanding problems in microfluidic DNA diagnostics: the need for a method compatible with "lab-on-a-chip platforms that can detect DNA target molecules in real time. The major accomplishment in this effort has been the development of a fluorescence based DNA microfluidic assay that does not require labeling of DNA samples. Additional information on these results in given in an article given below.

Awards and Recognition

In FY04 several Division staff members received the following recognition and awards:

Michael J. Tarlov – in recognition of outstanding advances and contributions to the science and technology of self-assembled monolayers, a vital infrastructural chemical system for the fields of chemical and biological sensing, nanoscience, and nanoengineering.

Mark A. Sobolewski – in recognition of major advances in electrical measurement methods and mathematical models for characterization of gaseous plasmas vital to the fabrication of microelectronic chips by the semiconductor industry

Title: New Hydrocarbon Liquid Flow Standard for 0.2 to 5 L/min

Authors: *T. T. Yeh, P. I. Espina, and J. Aguilera*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Improve NIST capabilities to provide users of turbine engines with flow measurement standards capable of supporting high fuel efficiency performance testing.

Purpose: Improve the uncertainty of NIST hydrocarbon flow standards by a factor of 5 or more.

Context: Turbine-based power plants are heavily used in ships, aircraft, large ground vehicles, and portable electric plants by both the U.S. Department of Defense and the commercial aircraft industry. Critical metrology requirements for these include methods to determine the performance of liquid flow meters used in turbine engine test stands. The testing of modern, high-efficiency engines requires uncertainties that have begun to exceed the capabilities of NIST's standards which currently have an expanded uncertainty of 0.12% of reading. This prompted the DoD Calibration Coordination Group to provide NIST with a grant aimed at developing a new generation of liquid hydrocarbon flow standards capable of providing traceability with uncertainties no larger than 0.025% of reading. The recently concluded three year program was a success, and today NIST has a new flow calibrator in our laboratory, Figure 1, designed to provide the requested performance. However, this performance is yet to be demonstrated.

With the support of the Department of Defense Calibration Coordination Group, NIST procured the new flow standards from Flow Dynamics Inc. of Phoenix, Arizona, currently the only manufacturer of such systems. Design features and specifications for the new flow standard were a collaborative effort between NIST staff and the private company. Upon receipt of the standard, NIST completed an extensive effort to establish direct traceability for the time, temperature, and length measurements that are inputs to the flow measurements. This included calibrating linear encoders that measure the stroke of the piston with a laser interferometer and tracing the piston cylinder diameter measurements through proving rings traceable to the Precision Engineering Division of NIST. A detailed uncertainty analysis for the flow standard was written and tests were conducted to validate its conclusions. The uncertainty and traceability documentation are essential elements in meeting the requirements of the NIST Quality System supporting calibration services.

Fig. 1. A dual rotor turbine meter is installed in the test section of the 2 L Hydrocarbon Liquid Flow Standard.

Major Accomplishment: Measurement uncertainty for hydrocarbon liquid flows has been reduced by more than a factor of ten to 0.01% (k=2). The 2 liter-capacity hydrocarbon liquid flow standard measures the performance of flow meters using type II hydrocarbon calibration fluid which simulates meter characteristics in

jet fuel by closely matching fluid viscosity and density values. The new flow standard replaces a gravimetric system over the range of 0.2 to 5 L/min. It utilized a volumetric displacement method, often termed a piston prover, as its basis of operation. The system operates unattended; the operator specifies flow set points, the standard steps through them accumulating system and meter under test data and stores these for later analysis and calibration report generation. This automation will reduce data transcription errors and the cost of calibrations for our customers.

Impact: NIST hydrocarbon flow measurement standards support the needs of aircraft turbine engine manufacturing requirements for improved fuel efficiency, supporting military and commercial user requirements.

Future Plans: Next we will procure a 20 L Hydrocarbon Liquid Flow Standard and characterize it to cover flows from 2 to 50 L/min. Ultimately, we will replace the gravimetric primary standard that has served this calibration service for thirty years, but is now outdated.

References:

1. Yeh, T.T., Espina, P. I., Mattingly, G. E., Briggs, N. R., and Aguilera, J., An Uncertainty Analysis of a NIST Hydrocarbon Liquid Flow Calibration Facility, Proceedings of the 2004 Heat Transfer / Fluids Engineering Summer Conference, Charlotte, North Carolina, USA, July 11-15, 2004.

Title: Exploratory Research Project: Sonic Nozzles as Primary Standards

Authors: *J. D. Wright and A. N. Johnson*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Provide state-of-the-art data to validate the theoretical models that predict sonic nozzle discharge coefficients.

Purpose: The ISO-9300 standard is predicated on a model that predicts the discharge coefficient value for convergent-divergent nozzles of a specific geometry that are operated at conditions resulting in sonic gas velocities through the nozzle throat, so called sonic nozzles or critical flow venturies (CFV). This model is currently validated at the 0.5% accuracy level. Use of NIST's world-class gas flow standards, with uncertainties ranging from 0.05% to 0.13%, coupled with accurate dimensional characterization of nozzle geometries, provides the opportunity to determine discharge coefficient data at previously unattained performance levels. Validation of ISO-9300 will greatly facilitate inexpensive, portable, and accurate gas flow measurements in industrial settings. In many applications users could have a sonic nozzle manufactured with a well characterized throat diameter and shape and use discharge coefficient values predicted by ISO-9300 to calculate flow from the nozzle.

Context: Critical flow venturis, often termed sonic nozzles, are widely used as gas flow standards by industry, are recognized as perhaps the most precise gas flow meters available today, and are the basis for metering gas flows over a very large range. Prior studies at NIST and other flow laboratories have shown that sonic nozzles maintain their calibration stability for more than 30 years within 0.2%. The ISO-9300 standard documents procedures for calculating flow from nozzles at the 0.5% relative uncertainty level via theoretical discharge coefficients. Because the dominant contributor to uncertainty in tests of sonic nozzle performance was the primary systems used to calibrate them, recent improvements in NIST primary standards allow much better

validation of the theoretical calibration predictions. This will have a significant impact of flow measurement accuracy in industries where sonic nozzles are used as primary flow standards.

Accomplishment: Calibrations of a set of sonic nozzles have been completed using our new 34 L, 677 L, and 26 m^3 *PVTt* primary gas flow standards, having uncertainties ranging from 0.05% to 0.13%. Additionally, the NIST Precision Engineering Division made nozzle shape and throat diameter measurements with uncertainty of 1 micron. The dimensional and experimental flow data were compared with the results of theoretical models and the agreement was excellent (<0.05%). This work validates much of the theoretical discharge coefficient predictions upon which ISO-9300 is based, in addition to identifying limitations of the model. It also identifies applications where users must exercise caution when using nozzles without flow calibrations. The results also show the importance of using the true nozzle shape, including the ratio of the throat radius to the radius of curvature, Ω, in calculating the discharge coefficient from the model.

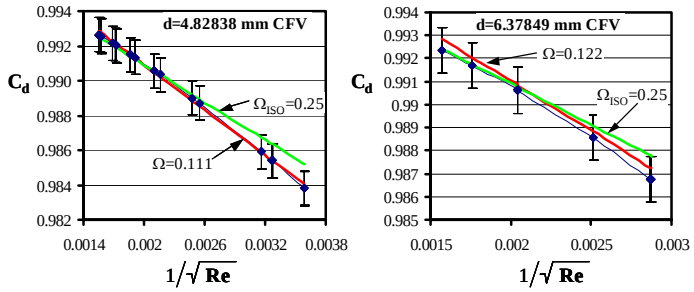


Fig 1. Experimentally determined discharge coefficient (symbols) and theoretical predictions. (Error bars on experimental data are ± 0.1 %)

Impact: Provide industry with simple, portable, and inexpensive gas flow measurement standards having accuracies competitive with those presently achieved in many National Metrology Institutes. The approach extends to flows that are too large to measure by conventional primary standard designs.

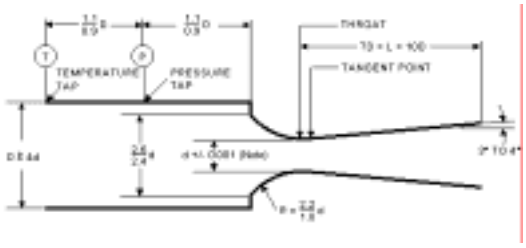


Fig. 2. Nozzle geometry parameters

Future Work: Extend this effort to smaller flows and smaller nozzle diameters where dimensional metrology capabilities are rapidly improving and we have extensive nozzle calibration data. We will also study the significance of nozzle shape defects, dirt deposited by flow, and unusual gas properties in causing departures from the expected flow behavior.

References:

1. ISO 9300:1990 (E), "Measurement of Gas Flow by Means of Critical Flow Venturi Nozzles," ISO/TC 30, Measurement of Fluid Flow in Closed Conduits.
2. Johnson, A. N., Wright, J. D., Moldover, M. R., and Espina, P. I., Temperature Characterization in the Collection Tank of the NIST 26 m3 PVTt Gas Flow Standard, Metrologia, 40, 211–216, 2003.
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4. Tang, S. P., Theoretical Determination of the Discharge Coefficients of Axisymmetric Nozzles under Critical Flows, Technical Report PR-118-PU, School of Mechanical Engineering, Purdue University, Lafayette, Indiana, 1969.

Title: Identification of Chemical Warfare Agents Using Temperature Programmed Microsensor Arrays

Authors: D. C. Meier, J. Evju, R. E. Cavicchi, S. Semancik (CSTL) and Z. Boger (Israel AEC)

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Develop advance sensing approaches for gas phase chemical compounds of interest in military and homeland security applications.

Purpose: Develop microsensor technology and signal processing methods to reliably and quickly detect low concentrations of chemical warfare agents.

Context: Reliable and sensitive detectors for chemical warfare (CW) gases are needed to aid in protecting both military personnel and civilians. Micro-sensors have great potential in this area, particularly if they respond reliably and quickly, are inexpensive, consume little power, and are far more practical for widespread use than large, complex analytical instruments. We are developing microsensor technology with many of these features for fast CW agent warning. Our conductometric micro-sensors are micro-electro-mechanical systems (MEMS) that are fabricated at NIST. Unique aspects of our microsensor research are that devices consist of arrays of microhotplates, each about the width of a human hair, that allow temperature-programmed operation of the sensors and redundant operation to reduce false positives. In addition, artificial neural network (ANN) signal processing methods are used to analyze data. This project has been supported in part by the Departments of Defense and Homeland Security.

Major Accomplishment: We have demonstrated that microsensor arrays can rapidly identify three chemical warfare (CW) agents and a CW agent simulant by analyzing the electrical responses of four microhotplate conductometric sensor arrays having elements with tin oxide and titanium oxide thin sensing films (see Figure 1). The measurements were done at the Edgewood Chemical and Biological Center (ECBC) on the CW agents sulfur mustard (HD), sarin (GB), tabun (GA), and chloroethyl ethyl sulfide (CEES), a sulfur mustard simulant. Analyte concentrations from nano-mol/mol (ppb) to micro-mol/mol (ppm) were determined. The microsensor arrays were trained to recognized and quantitate the agents by exposing them to each CW agent at four different known concentrations and twenty different operating temperatures. In addition, a blank response was obtained by exposing the arrays to dry air at different microsensor temperatures. All these data were used to train the neural network so that it could recognize each agent signature relative to a dry air background. The total time needed for scanning the sensor temperature, collecting response observations, and performing the ANN data analysis is about 15 seconds. Since detection time is critical in CW agent monitoring, we investigated a method called recursive elimination that allows the scan time to be decreased, while still allowing for accurate identification and quantification

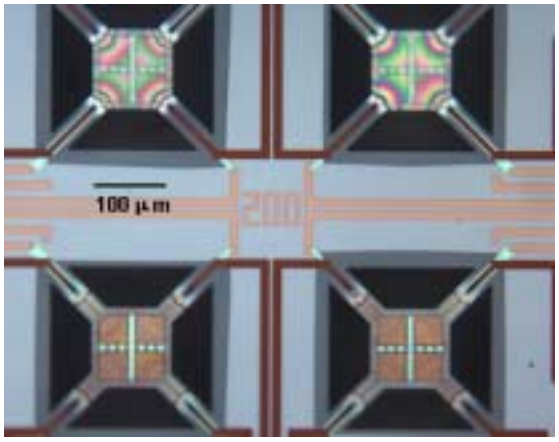


Fig. 1. Image of a microarray device with two TiO_2 (top) and two SnO_2 (bottom) sensing elements. (The color variations and banding reflect differences in oxide film thicknesses that are the result of temperature gradients that affect CVD deposition rates.)

of agents. The information obtained through Through this "pruning" process we have found that the micro-sensor scan time can be cut by 40% to 80%. Finally, recent results show that we are able to identify low concentrations of warfare agents and simulants even when the micro-sensors are exposed to interferences such as diesel fuel and water vapor at concentrations that are 10^4 to 10^6 times higher than the target species.

Similar research is underway to detect other chemical species to demonstrate the versatility of the micro-sensors for a variety of applications including industrial process monitoring, and breath analysis for disease diagnosis and bio-metric identification.

Impact: We have demonstrated that a microhotplate-based conductometric sensor array together with ANN models can rapidly and reliably identify the trace presence of different CW agents and yield their concentrations. The information obtained through pruning allows one to select appropriate sensing materials and operational programs to significantly reduce detection times.

Future Plans: Further experimentation will be conducted at NIST and ECBC to develop new databases that will allow us to examine the reproducibility and long-term stability of the devices, and the robustness of our approach against a wider range of interferences.

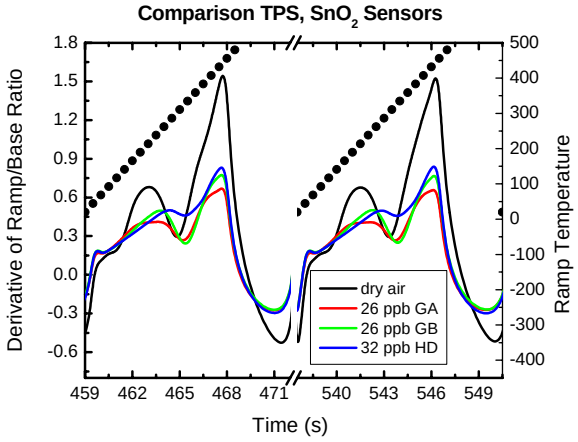


Fig. 2. Deriatives of temperature programmed sensing data from SnO_2 microsensors that has been used to recognize various chemical warfare agents.

Title: High Performance Oxide and Polymer Nanostructures for Advanced Solid State Chemical Microsensors

Authors: *K. D. Benkstein, C. J. Martinez, G. Li*, D. C. Meier and S. Semancik (CSTL)*
T. Mallouk (Pennsylvania State University), V. Dravid (Northwestern University)

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Develop advanced sensing approaches for gas phase chemical compounds of interest in industrial and environmental applications.

Purpose: Develop nanoengineered materials for microsensors and microanalytical systems to increase sensitivity, selectivity and stability of chemical detection and monitoring.

Context: Efforts underway at NIST, and through collaborations with two universities, are aimed at developing nanoparticles, nanofibers, nanowires, nanotubes, and related structures of oxides and polymers for use in nanosensor arrays and microanalytical systems. These nanomaterials are being studied as signal transducers for chemical sensors and as elements for filtering and preconcentration of analytes prior to detection. The approach is to assemble hierarchical structures for chemical sensing applications from single nanostructures and various nanocomposite materials. These well-defined nanostructures will increase the surface area and active interfacial sites for adsorption and reaction of gas phase analytes, thereby leading to more sensitive chemi-

cal measurements. These structures are also designed to enhance diffusion of the target molecules to functional sites by introduction of various scales of micro- and nano-porosity.

Major Accomplishment: Specific materials forms being studied include SnO_2 micro-shells, TiO_2 nano-particles, porous SiO_2, nano-fiber and nano-wire polyaniline, nano-wire oxides, and pure and doped SnO_2 sol gels dispensed by dip pen nanolithography. The SnO_2 micro-shells are formed via a solution phase, layer-by-layer deposition of SnO_2 nano-particles on sacrificial polystyrene spheres. These solutions are deposited on microhotplate platforms and the polystyrene spheres are removed by rapid heating to leave hollow, nano-porous SnO_2 shells with ultrathin walls (see Figure 1). The microhotplate also provide electrical contacts to the SnO_2 micro-shells for chemical sensing measurements. The SnO_2 micro-shells have exhibited increased sensitivity as high as 50 for detecting 1000 ppm concentrations of methanol in air. Porous silica is being developed as a high area support material for microscale preconcentrators and filters. Heating silsesquioxane/block copolymer blends to produce a highly porous SiO2 structure forms this meso-porous material. While much of our sensing research has focused on semiconducting oxides, conducting polymers are also now being investigated to expand the range of analytes that can be sensed by multi-element micro-arrays. We have found that polyaniline nano-fibers respond more than seven times faster than denser polyaniline films, and through a collaboration with PSU, we are exploring the sensitivity and speed enhancements possible with polyaniline nano-wires. Nano-wires and nano-tubes of polyaniline, SnO_2, and TiO_2 are all being studied as fundamental building blocks for constructing nano-arrays capable of analyzing complex chemical mixtures. Related oxide materials are being investigated with NWU, where dip pen nanolithography has been employed to pattern SnO_2 nano-materials.

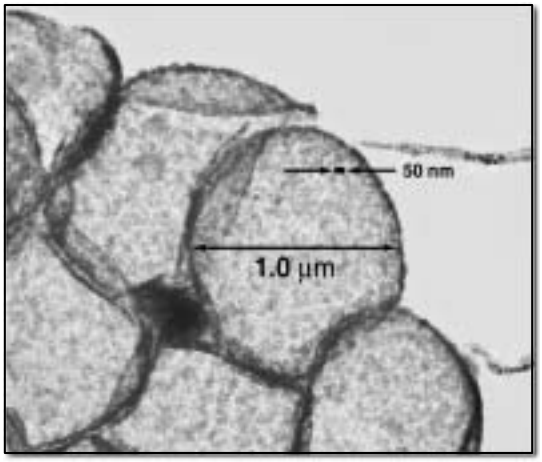


Fig. 1. TEM image of a SnO_2 micro-shells formed on sacrificial polystyrene spheres with layer-by-layer assembly of nano-particles

Impact: Higher sensitivity, stability, and reproducible fabrication of sensing materials are critical to next-generation sensing devices. The improved sensitivity, selectivity, and response-time that can be attained by proper assembly of nano-building blocks is expected to impact many application areas including alarm triggers for counter-terrorism, trace gas detection in space exploration, and the monitoring of gaseous biologically-generated compounds for medical diagnostics.

Future Plans: Future studies at NIST and at collaborating institutions will develop more reproducible processing methods and explore the fundamental mechanisms responsible for sensing enhancements realized through nano-engineering. Methods of manipulating nano-structures, particularly single particles, wires and tubes, onto micro-device platforms to enable electrical, and hence sensing, measurements, remains a challenge and will also be a focus of our studies.

Title: Investigation of Nano-wires for Chemical Sensing

Authors: *Richard E. Cavicchi, Christopher B. Montgomery (836) and Prahalad M. Parthangal, Michael R. Zachariah (University of Maryland)*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Develop advanced sensing approaches for gas phase chemical compounds for advanced sensing applications.

Purpose: To use nano-wires and nano-materials to create a new generation of chemical sensors with enhanced sensitivity and chemical selectivity

Context: Nano-wires (NW's), defined as electrically conducting structures with cross-sectional dimensions on the nanoscale, possess unique characteristics that make possible a host of new chemical sensing devices. Nano-wires have a high fraction of their constituent atoms on the surface and therefore have electrical properties that are exquisitely sensitive to the chemical environment. The high aspect ratio of NW's is also useful for producing high electric fields at the tips providing enhanced field emission that may be utilized for species-dependent ionization of gases. While carbon nano-tubes (CNT's) are an example that have received much attention, it is now possible to make NW's of other materials ranging from semiconductors such as Si, CdTe, or ZnO to a variety of metals. To realize chemical sensors, methods of synthesis of NW's must be developed that are compatible with integration onto chips. Sensing approaches that take full advantage of the unique properties of these materials must be developed.

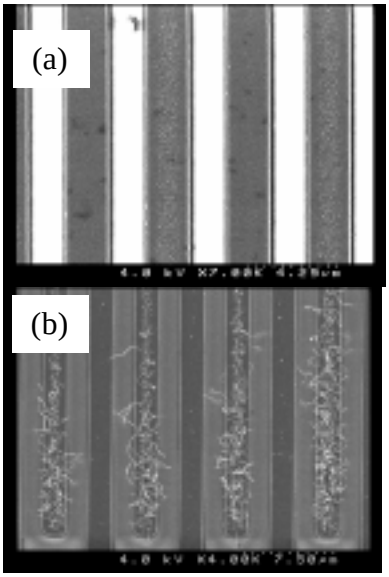


Figure 1. a) Particles localized on one set of interpenetrating comb electrodes. b) CNT's grown on one set of comb electrodes.

Approach: We have pursued two methods for fabricating nano-wires on sensor chip platforms. The first method takes advantage of recently developed methods for growing CNT's and NW's that start with a nanoscale metallic particle. For CNT's a chemical vapor growth is performed using a mixture of hydrogen and a carbon-containing species, such as methane, acetylene, or ethanol, with the substrate held at temperatures from 600 °C to 1000 °C. Nucleation occurs on the metal particle. For NW's the process is similar, but with different precursors. Novel to our approach is a vapor phase synthesis that produces charged nano-particles in an argon stream. Electric fields are used to size-select the nano-particles and guide their deposition to specific locations on a substrate. Figure 1 a) shows an example of the use of an applied electric field on one of the pair of interdigitated comb electrodes to localize the deposition of Ni particles to one electrode, and 1b) shows CNT's localized to one electrode, produced by CVD of acetylene using the Ni particles as nucleation sites.

A second growth technique for nano-wires takes advantage of our recent discovery that tungsten, when heated in the presence of a reducing gas, undergoes a significant change in morphology. We have developed a process for producing NW's of tungsten by a simple hydrogen plasma treatment of thin film or bulk tungsten which uses a much lower temperature 450 °C than is required for the vapor deposition methods described above. Thin films of tungsten treated in this

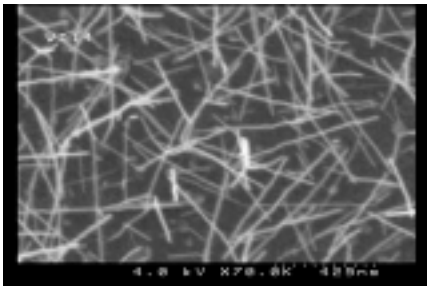


Fig. 2. Tungsten nanowires.

way are converted to NW "grass" as show in Figure 2 We have found that treatment of smooth tungsten filament wire results in a bristle coating of NW's which may also be useful for field emission applications. Tests have shown these NW films to be sensitive to volatile organics.

Results and Future Plans: We are currently exploring treatments of the nano-wires, including templated growth of other materials on CNT's and NWs. We are exploring the limits of field-guided deposition of nano-particles, including a novel self-assembly approach that uses the concentration of electric fields at the tips of NWs. These new materials will be integrated with existing silicon micromachined sensing platforms in our group to perform chemical sensing via electrical measurements at a wide range of temperature.

Title: DNA Detection in Microfluidic Channels

Authors: *R. A. Zangmeister, and M.J. Tarlov*

CSTL Program: Health and Medical Products

Vision: Develop advanced sensing approaches for applications in biological and chemical systems.

Purpose: This project addresses one of the outstanding problems in microfluidic DNA diagnostics: the need for a method compatible with "lab-on-a-chip platforms that can detect DNA target molecules in real time.

Abstract: To meet the need for real-time DNA detection in microfluidic systems, a unique fluorescence based DNA microfluidic assay was developed that does not require labeling of sample DNA. The assay is based on the displacement of a short sacrificial fluorescent-tagged DNA strand by a longer untagged DNA sample, or target, strand as it is electrophoretically transported through a DNA-containing hydrogel plug immobilized in a microfluidic channel. The assay is rapid and does not require labeling of sample DNA.

Major Accomplishments: The major accomplishment on this project for FY04 was the development of a fluorescence based DNA microfluidic assay that does not require labeling of DNA samples. This assay is designed for real time monitoring of nucleic acid solutions by the electrophoresis of sample DNA through hydrogel plugs formed in a microfluidic channel. The main procedures of the assay are illustrated in Figure 1 (top). A DNA probe sequence designed to recognize a target DNA strand is chemically tethered in a hydrogel plug formed in a microflu-

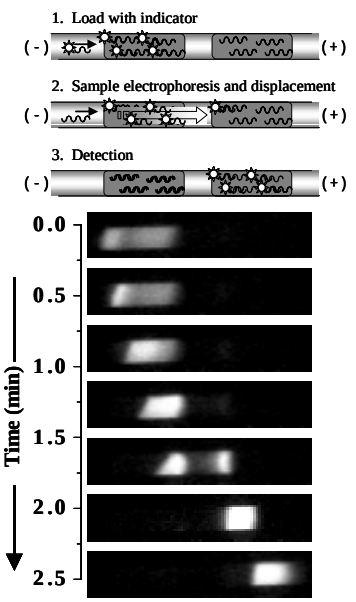


Fig. 1: Design of displacement assay (top) and corresponding fluorescence data of displacement assay imaged over 2.5 min (bottom).

idic channel. A short, fluorescently tagged indicator sequence is hybridized with a portion of the probe sequence (step 1), forming a stable duplex under the conditions used for the assay. The DNA sample to be analyzed is driven through the hydrogel by applying an electric field along the microchannel. If the target DNA strand is present, it binds to the entire probe sequence and displaces the indicator sequence (step 2). The displaced fluorescently tagged indicator sequence is then driven by the electric field into a second hydrogel located downstream where it is captured and detected (step 3). Figure 1 displays an actual analysis of a solution containing a random 20-mer DNA target strand. In this analysis the 20-mer strand displaces a 10 mer indicator sequence (Figure 1, bottom). The displacement event signals the presence of the 20-mer target in the analyte solution. No displacement is seen when a mismatched target strand of equal length is used.

Impact: This approach to DNA assay explores new detection method for compounds where fluorescent tagging in not possible, e.g., detection of toxic metals such as lead, in blood samples. This work has been presented at several conferences including the Gordon Conference on Microfluidics and microTAS 2003. A manuscript describing the assay has been published in Analytical Chemistry (**2004**; *76*(13); 3655-3659).

Future Plans: Because of the success of this assay, other hydrogel-based assays are being explored including the incorporation of catalytic DNA molecules that sense toxic lead ions in water.

Title: Outreach Activities in Thermometry

Authors: *D.C. Ripple, K.M. Garrity, C.W. Meyer, G.F. Strouse, W.L. Tew, C.D. Vaughn*

CSTL Program: Industrial and Analytical Instruments and Services

Purpose: The NIST Thermometry Group strives to maintain world leadership in thermometry, and to provide our users with all of the tools to attain traceability to NIST standards. Research activities alone cannot achieve this goal. Outreach activities by the Thermometry Group provide visibility of our work, a mechanism for training and education of users, and a forum for cooperation and exchange of ideas with other scientists.

Major Accomplishments: For many decades, the NIST Thermometry Group has offered the Precision Thermometry Workshop at its Gaithersburg campus, and we continued this tradition in 2004. We have developed a number of additional training classes that complement the overview provided by the Precision Thermometry Workshop. At the 2004 Measurement Science Conference, we presented a newly developed workshop on the "Selection, Calibration, and Use of Contact Thermometers." To provide more extensive hands-on training, we are developing a series of small workshops that provide intensive laboratory instruction on particular techniques, using the highest quality of equipment available at NIST. We have held the ITS-90 Fixed-Point Cell Miniworkshop for several years, and last year a new workshop on Liquid-in-Glass Thermometers was added.

Recently the number of laboratories seeking accreditation in the field of thermometry has significantly increased. Many of these laboratories claim uncertainties comparable to those of many National Metrology Institutes. Staff from the NIST Thermometry Group have increased our efforts in accreditation activities by a) serving as technical assessors, through the National Volun-

tary Laboratory Accreditation Program (NVLAP), of laboratories claiming low levels of uncertainty, b) creating guidelines of appropriate levels of proficiency testing, c) designing and conducting proficiency tests, and d) assisting companies in meeting accreditation requirements in foreign countries. The expertise of NIST staff is an invaluable resource for companies seeking accreditation, and our involvement helps to ensure that accreditation is a reliable indicator of quality.

We continue our involvement with Standards Development Organizations such as IEC, ASTM, and ASME. For example, NIST staff members have presented invited talks to ASTM committee E20 on Thermometry for each of the last three years.

Impact: Because of our outreach activities, the members of the NIST Thermometry Group are a world-renowned source of thermometry expertise. Several secondary calibration laboratories in the U.S. have attained a level of competence in thermometry that is commensurate with many foreign National Metrology Institutes, partly because of ready accessibility to methods established at NIST.

Future Plans: Future outreach activities will address the specific needs of particular industrial sectors. For example, workshops previously held in conjunction with a conference on semiconductor processing and with the ASTM committee on petroleum have led to requests for preparation of training materials for use in these industries.

Title: Uncertainties of Industrial Thermometers

Authors *K.M. Garrity, D.C. Ripple, G.F. Strouse, C.D. Vaughn*

CSTL Program: Industrial and Analytical Instruments and Services

Purpose: Provide new and improved methods to evaluate industrial thermometer performance.

Context: In spite of the maturity of commonly used industrial thermometers, including thermocouples, resistance thermometers, and liquid-in-glass thermometers, the uncertainty of these thermometers in calibration and in use is often ill documented resulting in significant error in defining calibration interval requirements or sensor replacement. Both of these is very costly to many end-users. The market for industrial thermometers is large: approximately $100 million per year for resistance thermometers and $280 million per year for thermocouple devices. To support the effective use of these thermometers in industry and government, the NIST Thermometry Group is conducting an ongoing project in sensor characterization.

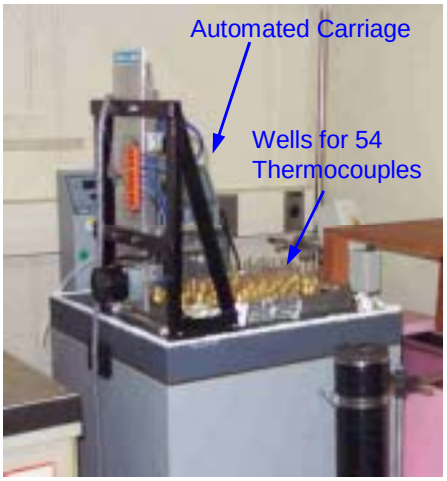


Fig. 1. Stirred oil bath for the determination of long-term drift of thermocouples at 200 °C. The carriage allows thermocouple testing under continuous thermal cycling by automated insertion and withdrawal into the bath.

Major Accomplishments: Recent performance evaluation tests of two types of industrial thermometers have been completed. Because thermocouples are often installed in elevated temperature environments for long pe-

riods of service, we have recently focused on documenting the drift characteristics of these sensors at elevated temperatures. In one set of tests, the drift of common base-metal thermocouples was measured over one year at a temperature of 200 °C (see Figure 1). The observed drift rates (as large as 0.3 °C over one year for a fixed installation depth, and as large as 1 °C for variable depth) are highly predictable. Thus, the results of this study can be used to establish periodic replacement intervals in industrial applications, eliminating the need for expensive, and often impractical, periodic calibrations. In another set of tests, we determined the drift of thermocouples during the act of calibration. This drift is a key component in the calibration uncertainty that is often neglected in industry, resulting in an unrealistically optimistic calibration uncertainty. For liquid-in-glass thermometers, previously published repeatabilities had no clear statistical basis. We recently completed a study of the repeatabilities and calibration uncertainties of a selection of 18 liquid-in-glass thermometers over the range –20 °C to 400 °C. The results demonstrated that the now-obsolete published repeatabilities were a factor of 2.5 too large.

Impact: NIST methodology developed for testing of industrial thermometers is often adopted by industry, either by direct familiarity with NIST publications or by incorporation of NIST methods in consensus standards by ASTM or other organizations. The values obtained by NIST for repeatability and drift are trusted in industry as an impartial assessment of expected sensor performance. Performance testing results from well conceived experiments provide a basis for rational change in their use and in the standards supporting such use. It is anticipated that the results of this work, and similar efforts in the future, will become the basis for changes in documentary standards issued by ASTM and other standards development organizations.

Future Plans: For industrial resistance thermometers, sensor hysteresis (the dependence of the thermometer reading on its past thermal history) is one of the dominant components of the uncertainty of these devices in actual use, yet methods for measuring hysteresis are crude and non-standardized. We are planning an automated apparatus for characterization of this key property.

Title: In Situ Calibration of Lightpipe Radiometers for Rapid Thermal Processing (RTP) Between 300 °C to 700 °C

Authors: *K.G. Kreider, W.A. Kimes, D.C. Ripple, B.K. Tsai (Div. 844)*

CSTL Program: Microelectronics

Vision: Provide measurement standards and advanced measurement methods supporting metrology needs of the semiconductor industry.

Purpose: Develop silicon wafer-based artifacts suitable to RTP tools suitable for the accurate calibration of radiometric devices used for tool control.

Context: Accurate temperature measurements are critical in rapid thermal processing (RTP) of silicon wafers for thermal oxidation and dopant anneals. Many RTP tools use lightpipe radiation thermometers (LPRTs) to measure the wafer temperatures during processing. These LPRTs can yield accurate temperature measurements when they are calibrated *in situ* or calibrated *ex situ* and used with a suitable model to correct for surface emissivity and chamber irradiation effects. Recent developments of LPRT sensor technology have enabled measurements to temperatures below 300 °C, compared to a previous lower limit of 500 °C. Use at these lower temperatures requires extreme care due to the relative increase in background irradiation compared to the

weak signal produced by Planck emission from the wafer itself. This project was initiated to understand the metrology of *in situ* calibrations of LPRTs in this temperature region.

Major Accomplishments: NIST has been assessing the performance of commercial LPRTs and their calibration and temperature measurement uncertainty in RTP tools. We have developed highly accurate blackbody calibration techniques for the LPRTs; characterized and measured the temperature sensitivity of the LPRTs; developed technology for *in situ* calibration of the LPRTs in the RTP tools using the NIST patented thin-film thermocouple calibration wafer; and measured the effects of wafer emissivity and LPRT proximity on the LPRT measurements in the RTP tool.

New commercial LPRTs couple the optical detector directly to the lightpipe resulting in improved detectors for low levels of radiance. These cable-less lightpipe radiometers (CLRTs) are capable of measuring temperatures below 300 °C. Typical results of calibrating a CLRT against our NIST thin-film thermocouple (TFTC) calibration wafer from 315 °C to 700 °C in our NIST RTP test bed are shown in Figure 1. Below 550 °C, light leakage from the heating lamps of the RTP tool introduced a significant error in the LPRT readings. By measuring the transient response of the LPRTs following rapid energizing of the heating lamps, we were able to differentiate between the radiance of the wafer and ambient chamber light. This allowed us to correct for the ambient chamber light from the radiance of the wafer.

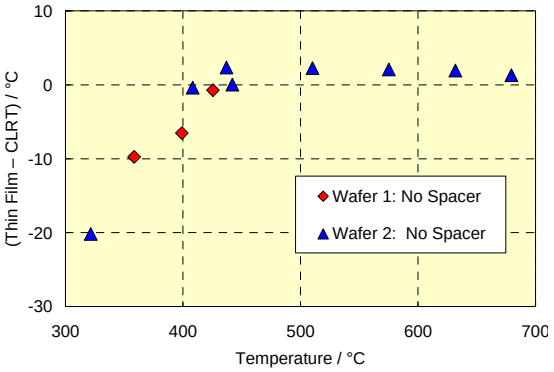


Fig. 1. Difference between wafer temperatures as measured by the NIST thin-film thermocouple wafer and as measured with a CLRT.

Impact: The results of this study, which reported the uncertainties attainable for an *in situ* calibration with and without correction of chamber irradiation effects, were published for and presented to the metrology and semiconductor fabrication industry responsible for RTP tools. This information assists manufacturers and users of RTP tools to significantly improve the uncertainty of their temperature measurements. This lightpipe study follows our previous work relating to *in situ* and *ex situ* calibration of the lightpipe radiation thermometers for RTP temperature measurements. The RTP project, funded by the NIST Office of Microelectronics Program and guided by our Common Interest Group from the semiconductor processing industry, has focussed on assisting industry in improving temperature measurements to meet the needs identified in the International Technology Roadmap for Semiconductors.

Future Plans: Future work is focused on the development and characterization of sensor technology for *in situ* calibration wafers. We are engaged in developing resistance sensors for use in the range 300 °C to 650 °C, where RTP tools are used in the formation of silicides and existing reference sensors are either fragile or unstable. We are also evaluating the sensitivity of commercial calibration wafers to perturbing heat fluxes.

Title: Evanescent Wave Cavity Ring-Down Spectroscopy (EW-CRDS) of Surface Hydroxyl Groups on SiO_2

Authors: A.C.R. Pipino, I.M.P. Aarts (Eindhoven University of Technology, The Netherlands)

CSTL Program: Technologies for Future Measurements and Standards

Purpose: Demonstrate EW-CRDS detection capabilities as a probe and diagnostic tool for investigating chemistries at interfaces.

Context: The SiO_2 surface is ubiquitous in science, technology, and the environment. Whether used as a catalytic or chromatographic support or as the substrate for atomic layer deposition, the SiO_2 surface displays reaction chemistry that is largely controlled by the presence of surface silanol (SiOH) groups. Yet ambiguous results are often obtained in spectroscopic studies of silica gels or powders, which increase surface area to enable detection of the weak surface SiOH signals. To realize a decisive diagnostic probe of the planar SiO_2 surface, we use evanescent wave cavity ring-down spectroscopy (EW-CRDS) that is a variant of the gas-phase CRDS technique employing a miniature, ultra-low-bulk-OH fused-silica optical resonator with total-internal-reflection (TIR) mirrors.

Major Accomplishments: Using EW-CRDS we have obtained vibrational combination band spectra of surface SiOH and adsorbed water on ultra-smooth amorphous silica in the 8000 cm^{-1} region. By obtaining spectra at both s and p polarizations, we are able to identify the dipole orientation of the SiOH group for each observed spectral peak. Remarkably, we find evidence for crystalline character for both SiOH and adsorbed water layers, where the latter suggests the formation of an ice-like structure at room temperature. In Figure 1, the combination band spectra for an OH mode of surface SiOH under dry nitrogen gas is shown for s and p polarizations (black and blue lines, respectively). Note that the maximum optical loss for these weak surface spectra is only 2×10^{-6}, which illustrates the very high sensitivity of EW-CRDS. Moreover, two SiOH bands are observed, which are both *highly polarized*. The p-polarized (8118 cm^{-1}) band indicates a mean orientation for the transition dipole that is perpendicular to the surface plane, while the s-polarized (8152 cm^{-1}) band indicates a parallel transition moment. Such spectra are consistent with the existence of a crystalline surface phase, similar to a facet of crystalline silicon dioxide. In Figure 2, one of four adsorbed-water peaks is shown. Under dry nitrogen (no previous heating, black line), adsorbed water is still present due to rather strong hydrogen bonding with the surface SiOH groups. Exposed to 10% relative humidity (blue line), the water band increases strongly and sharpens slightly. However, when exposed to 50% relative humidity, the water band shows only a slight additional increase by contrast, suggesting the band intensity saturates at one-monolayer coverage. Furthermore, this band and the three

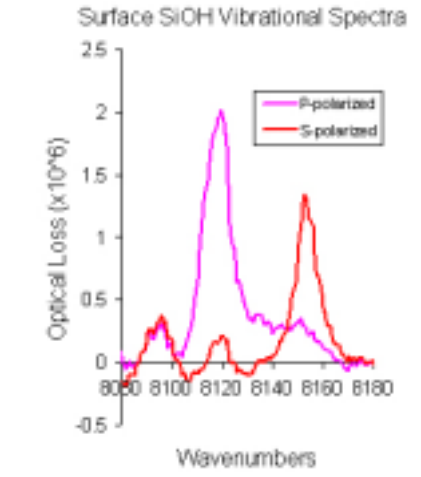


Fig 1. S and P OH mode polarized absorption spectra for SiOH.

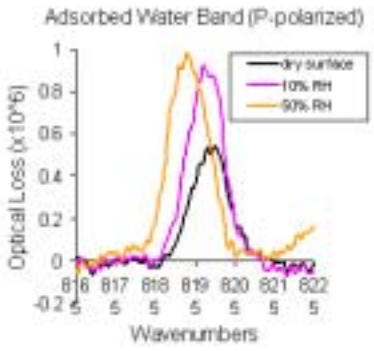


Fig. 2 Shifts in water absorption on SiO_2 surfaces.

other observed adsorbed-water bands are also highly polarized, indicating an ordered water layer supported by the underlying ordered SiOH layer. The existence of an ice-like layer on silica at room temperature has also been inferred from sum-frequency generation (SFG) measurements and predicted in recent theoretical studies. EW-CRDS provides detailed surface structural information with the potential for absolute surface coverage and absolute surface reaction rate determinations.

Future Plans: This work is part of an on-going collaboration between NIST and the Eindhoven University of Technology (TU/e) in the Netherlands. Originally developed at NIST, EW-CRDS is currently being used by the group of Richard van de Sanden in the Applied Physics Department at TU/e to probe thin-film structure and growth processes, including growth of amorphous, hydrogen-doped silicon and atomic-layer-deposition processes. Other current applications of EW-CRDS involve studies of the liquid/silica interface and novel size-selected nanoparticle catalysts.

Title: The NIST Hybrid Humidity Generator

Authors: *G. Scace, C.W. Meyer, W.W. Miller, J. Hodges, D. Ripple*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Provide state-of-the-art standards and dissemination methods for humidity measurements

Purpose: Develop new approaches to measurement standards for moisture in gases that enhance NIST measurement services provision.

Context: NIST performs humidity calibrations for customers as part of its mission to develop, maintain and disseminate measurement standards. Gas streams of well-characterized humidities are generated for calibration of customer's hygrometers. The NIST Hybrid Humidity Generator has been designed to extend the humidity range provided by NIST, increase operational safety and efficiency, decrease calibration uncertainties, and eliminate the need for expensive cryogenic cooling. The new upper limit of water concentration (0.6 mole fraction of water), or from a dew point of ~25 ºC to 85 ºC will improve NIST support of industrial applications such as fuel cells and food processing.

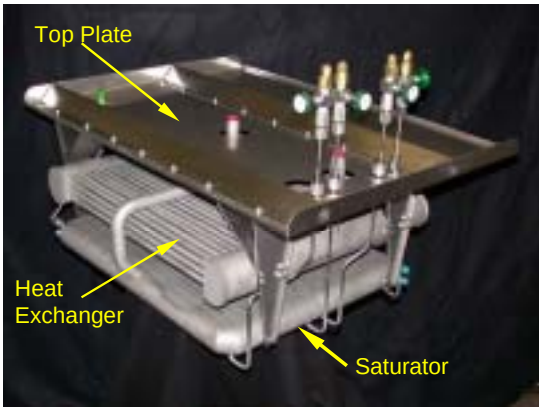


Fig. 1. Heat Exchanger and Saturator assembly –NIST Hybrid Humidity Generator. The top plate in a stirred water bath for optimal temperature control suspends the assembly.

Major Accomplishments: The NIST Hybrid Generator generates humidity using two distinct physical principles. First, because the vapor pressure of water is well established as a function of temperature, a gas stream can be saturated at a known concentration of water vapor by passing the gas through a saturator—a serpentine passage maintained at a known, uniform temperature that contains a layer of water on its lower surface. Second, for the creation of low moisture levels

(down to 3 ppm mole fraction), the gas exiting the saturator can be reduced in water concentration by diluting the gas stream with dry gas. Present day laminar-flow elements enable very accurate measurements of gas flow, resulting in low uncertainties of the water concentration of the diluted output stream. The use of a dilution scheme is very fast and efficient compared to operation of a saturator at cryogenic temperatures. Furthermore, a commercial pre-saturator initially brings the input gas to almost the desired moisture level, reducing the heat and mass transfer load of the saturator itself and allowing operation at high gas flow rates and high water concentrations. In FY04, the pre-saturator, heat exchanger, saturator assembly, and the dilution system were completed. The heat exchanger and saturator, core elements of the generator, are shown in Figure 1. To facilitate efficient operation, the new generator is designed to allow full automation of the pre-saturator, dilution system, and saturator baths. We have also designed the system to support closed-loop control algorithms, in which the performance of the saturator is continuously monitored and the pre-saturator adjusted to give minimum uncertainties in the generated humidity.

Future Plans: In FY05, the Hybrid Humidity Generator will be completed, its operation refined and automated, and its uncertainty documented. Use of the generator in regular calibration service is anticipated at the end of FY05.

Title: Testing of a Nanogate Device as a Variable Flow Leak Element

Authors: Patrick J. Abbott, Albert Lee (Div. 836); James White, (MIT)

CSTL Program: Industrial and Analytical Instruments and Standards

Purpose: Identify and utilize new technological approaches capable of improving low flowrate and vacuum standards.

Context: Many critical industrial processes rely on generating and delivering accurate and precise flows of gas. Examples include leak testing of nuclear containment vessels, gas delivery in semiconductor processing, quantifying the emission of ozone-depleting chlorofluorocarbons, food processing and packaging, and testing of medical implants such as pacemakers. The gas flows required for these applications span a very broad range, from as low as 10^{-14} moles per second to greater than 10^{-6} moles per second. Several types of measurement instruments are current used to cover this reange including mass flow controllers, metal capillary leak elements, and permeation leak elements are used to cover this flow range. Recently, a variable flow leak artifact using MEMS technology called the Nanogate, Figure 1, was developed at the Massachusetts Institute of Technology (MIT) and hold excellent potential for covering this range with a single device technology.

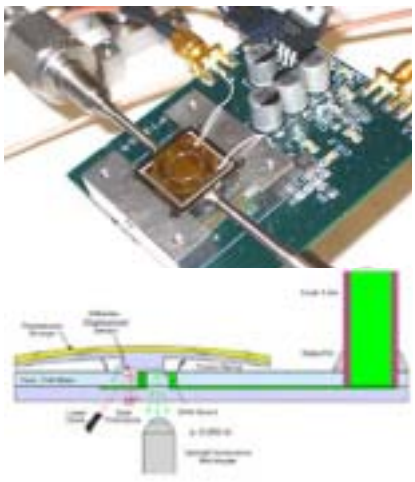


Fig. 1 The Nanogate Valve with side-view schematic

The Nanogate has the potential for generating gas flows over the entire range mentioned above, for many gas of interest, and offers the advantage of precise flow rate control

due to its ability to adjust its opening on a sub-nanometer scale using a picomotor actuator. The Nanogate is a micro-mechanical device that is designed to control a nanometer-sized gap. Precise control of the gate opening is accomplished by deflecting a cantilevered plate that is anchored by a torsion spring, as shown in the diagram below.

To characterize operational performance of the nanogate device, MIT researchers needed a way of generating accurately known flows of gas. The NIST Pressure and Vacuum Group maintains low gas flow standards over the range of 10^{-12} to 10^{-6} mol/s and can generate lower flows using a flow division technique. Initial testing of the Nanogate device with helium gas has agreed well with theory as shown in Figure 2. A roughly parabolic dependence between helium flowrate and applied picomotor opening was obtained, and minimum leak rate changes on the order of 10^{-13} mol/s were obtained for 7.5 psi of helium at the inlet. Additional testing is planned with other gases over the complete range of the NIST low gas flow standards. Given the fine resolution of the Nanogate opening, a minimum change in flowrate per applied pulse should be below 10^{-14} moles per second. This may make the Nanogate the most precisely controlled gas delivery valve in the world.

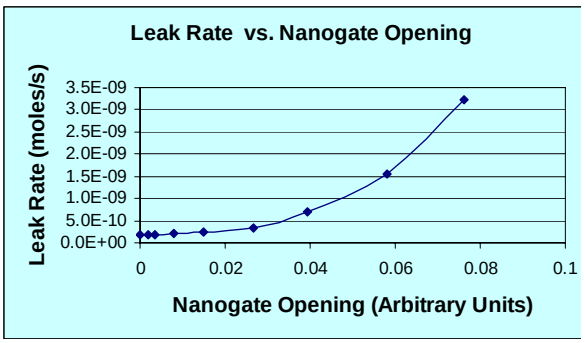


Fig. 2. Nanogate flow rate characteristics

Title: Progress Toward Realizing Pressure with Dimensionally-Based Piston Gauges

Authors: *J.W. Schmidt, A.P. Miiller, W.J. Bowers, and D.A. Olson (836)*

CSTL Program: Industrial and Analytical Instruments and Standards

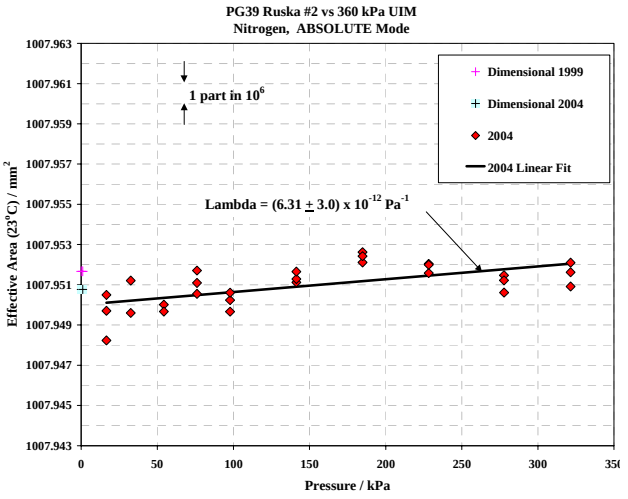
Vision: Provide World-Class Measurement Standards for Pressure through development of innovative approaches to realization of standards.

Purpose: Demonstrate performance levels of large diameter, piston/cylinder assemblies, i.e., piston gauges, whose areas are dimensionally determined, thereby providing a primary pressure standard.

Context: The goal of this work is to realize the unit of pressure, or the Pascal, in the atmospheric to high-pressure regime, and transfer the unit pressure to our customers. An accurate determination of pressure has many important applications, including altitude determination of aircraft, measurement of barometric pressure, and monitoring and control of pressure in manufacturing processes. The pressure standard for NIST in the atmospheric range is presently a mercury manometer. Piston/cylinder assemblies (*i.e*, piston gauges) are an alternative means for establishing pressure; through use of a variety of piston diameters and mass loads they can operate from the atmospheric range to several hundred MPa (tens of thousands of psi). Dimensional measurements allow a direct determination of the effective area of a piston gauge, and therefore the pressure it can generate, without reference to another pressure artifact for its calibration. The ability to measure the dimensions of the piston/cylinder assemblies that are extremely round and

straight have allowed us to contemplate piston gauge pressure standards whose uncertainties approach the best manometers. Realizing pressure by two independent techniques provides independent methods for realization of primary pressure standards more credence to the uncertainties claimed by each. At NIST an additional independent realization of the pressure unit provides a means to check the operation of our primary mercury manometers and a primary pressure standard having considerably greater operating range.

Major Accomplishment: For the last few years, NIST has been studying two 35 mm diameter piston gauges as potential primary standards, designated as PG 38 and PG 39. The artifacts have been used as check standards for the NIST Ultrasonic Interferometer Manometer (UIM) for the last decade. Those comparative measurements have shown PG 38 and PG 39 to be stable within a few parts in 10^6. This year, the piston and cylinder of both PG 38 and PG 39 were accurately dimensioned by Physikalisch Technische Bundesanstalt (PTB) and analyzed using a model of normal and shear forces on the base and flanks of the piston. PG 39 was also dimensioned by PTB in 1999, and these two sets of measurements have been used to evaluate the dimensional stability of the artifact and the repeatability of the dimensioning method.



Comparison of effective area of PG39 from NIST UIM, 1999 dimensional data, and 2004 dimensional data, showing agreement to 1 in 10^6.

The dimensional measurements indicate all four pieces are round to within ±30 nm and straight to within ±100 nm over a substantial fraction of their heights. Using the 2004 data, the model indicates an expanded relative uncertainty on the effective area of 4.4×10^{-6} for PG39. Operational effects, such as force determination under piston rotation, gas species, or gas mode, may increase the uncertainty when the artifact is used to generate pressure. The difference in the relative effective area between the 1999 and 2004 dimensional data for PG39 is less than 1×10^{-6}, and the difference between the 2004 dimensional data and a 2004 pressure comparison with the UIM is also about 1×10^{-6}.

Impact: Broadening NIST's pressure standards capabilities enhances it ability to provide state of the art measurement capabilities to its customers at levels that exceed the capabilities of many NMI's. Such capabilities provide U.S. instrument manufacturers capabilities with competitive advantage in global markets.

Future Plans: In the coming year, we will compare PG 38 against PG 39 to further verify the modeling technique, and propagate characterization of the artifacts to other piston gauge standards by direct calibration. This will revise the NIST pressure scale for gases up to 17 MPa, and provide lower uncertainties for our customers.

Title: Development of a Calibration System for Refrigerant Leaks

Authors: *Patrick J. Abbott (836)*

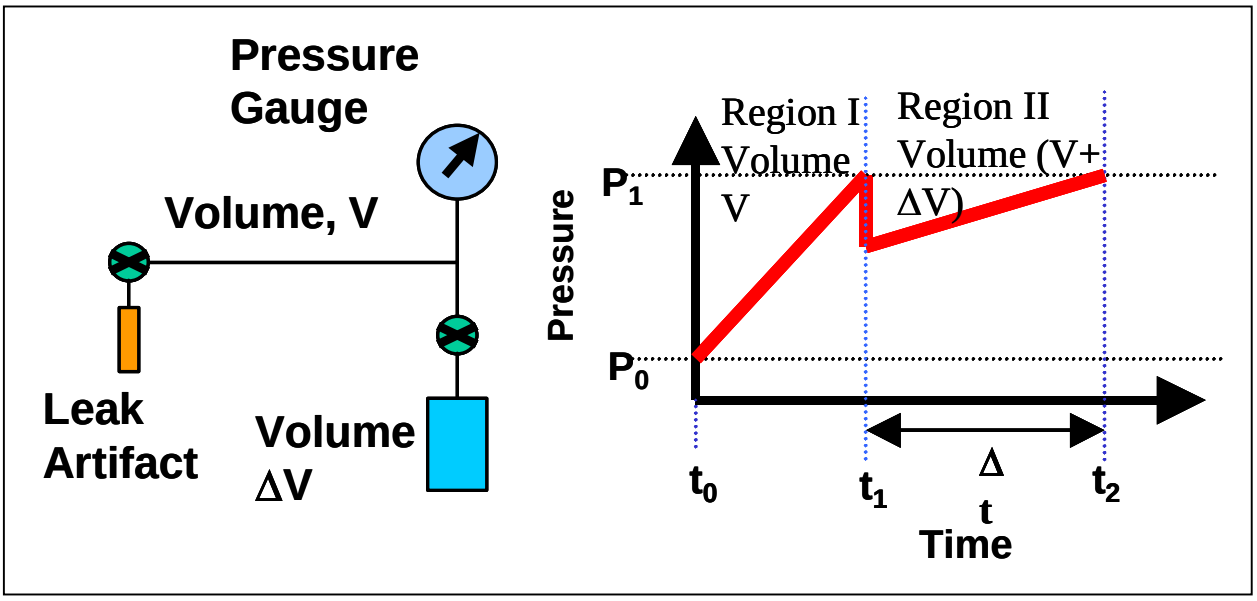
CSTL Program: Industrial and Analytical Instruments and Standards

Vision: Provide U.S. industry with new leak standards in a context consistent with their use.

Purpose: Provide U.S. refrigeration industry with new leak-to-atmosphere standards of significantly improved accuracy to support industry need to better quantify leakage quantities.

Context: In recent years, the detection of gas leaks in commercial and industrial refrigeration systems has become of paramount importance. Emissions of HFC (Hydrofluorocarbons) have been determined to contribute to environmental problems such as global warming. Many countries either limit or are considering placing limits on the emission of these and other types of refrigerant gases. In order to ensure compliance with emissions limitations, it is necessary to quantify leaks in cooling systems. This requires accurate calibration of refrigerant leak detecting equipment. In general, refrigerant leak artifacts are not very accurate due to the lack of availability of calibration standards. Recognizing this international need, the NIST Pressure and Vacuum Group has developed a calibration system for refrigeration leak artifacts that is specifically designed to account for their discharge into atmospheric pressure. Refrigerant leaks are detected using "sniffers" to probe suspected leaks, all done *in situ* at atmospheric pressure. This is in contrast to the more common leak detection technique that relies on evacuating the vessel of interest and using a mass-spectrometer based helium leak detector to find and quantify the leak.

The calibration system is based on the "Delta P Delta V" pressure rate-of-rise technique. This method measures the rate of pressure change inside sealed volumes in response to an inflowing source of gas (a leak artifact). The process is illustrated in the diagram below:



To calculate the flow rate of gas, it is only necessary to know the pressure rates-of-rise in Regions I and II, and the volume ΔV. Because the flow rate is measured at atmospheric pressure, the temperature of the calibration system is actively controlled to a few millikelvins in order to minimize components contributing to the overall performance uncertainty of the leak artifact under test.

In FY2004, final system parameters were characterized, and the calibration method was tested using a leak artifact that had been calibrated using the NIST Primary Vacuum Flow Standard. This test was performed under vacuum conditions because no atmospheric pressure leak standard was available; in spite of this, the results were a good indication of overall system performance. A helium leak artifact having a flow rate of approximately $4x10^{-11}$ moles per second at 23 ^{o}C was used, and the results obtained with the new calibration system were consistently within 2 % of this value. The uncertainty budget for the calibration system is approximately 5 %.

Impact: A new measurement standard capability serving the refrigeration industry standards of significantly increased accuracy.

Future Plans: Future plans include testing at atmospheric pressure with a refrigerant leak. This will be done in conjunction with a European National Metrology Laboratory that is concurrently developing a system based on a different measurement process for calibration of refrigerant leaks. Success of this stage will pave the way for a NIST calibration service for refrigerant leaks.

Title: Controlling "Injection Barriers" into Prototype Molecular Wires Through Substrate Coupling Chemistry

Authors: *S. W. Robey (Div. 837) and R. D. Van Zee & C.D Zangmeister (Div. 836)*

CSTL Project Area: Technologies for Future Measurements and Standards

Vision: Develop metrology tools necessary for the development of manufacturering capability of molecular electronic devices and components and use such capabilities to characterize candidate materials classes.

Purpose: Develop metrology tools that will underpin the development of molecular electronic materials and devices.

Context: The drive to introduce organic molecular materials into electronic device applications, (organic or molecular electronics) is motivated by a number of potentially attractive features, such as ease of fabrication, ability to fabricate on flexible substrates, and the wide extent to which organic materials can be functionalized via organic synthetic methods. A range of applications is foreseen for organic field effect transistors and light emitting diodes including, for instance, flexible displays and other low cost flexible electronics.

In addition to replacing inorganic semiconductors in more or less conventional device architectures, organic systems are also of interest in the more speculative, and potentially more revolutionary, area of “molecular electronics”. Here, it is envisioned that the nonlinear characteristics of individual molecules, or small ensembles, will provide the required device functionality, allowing low cost chemical synthetic methods to replace, at least partially, multi-billion dollar semiconductor fabrication lines in the production of nanoscale device structures.

In either application format, charge injection at a molecule-contact interface plays a vital role in controlling transport and, thus, potential device performance. Interfacial charge injection is dictated by chemical bonding. The resulting band line-up between the Fermi level of the contact and transport levels of the molecule. Information relating to band line-up is difficult to obtain using conventional techniques in the case of the single-molecule length-scale systems of interest in molecular electronics. We have employed a combination of one-photon (He I resonance excitation) and two-photon photoelectron spectroscopy, using sub-picosecond Ti:sapphire laser-based excitation, to determine the electronic structure, including injection barriers to both occupied and unoccupied levels, of oligio(p-phenylene-ethynylene)thiol (OPE) self-assembled monolayers, a system that has become a benchmark for theoretical and experimental studies in the area of molecular electronics.

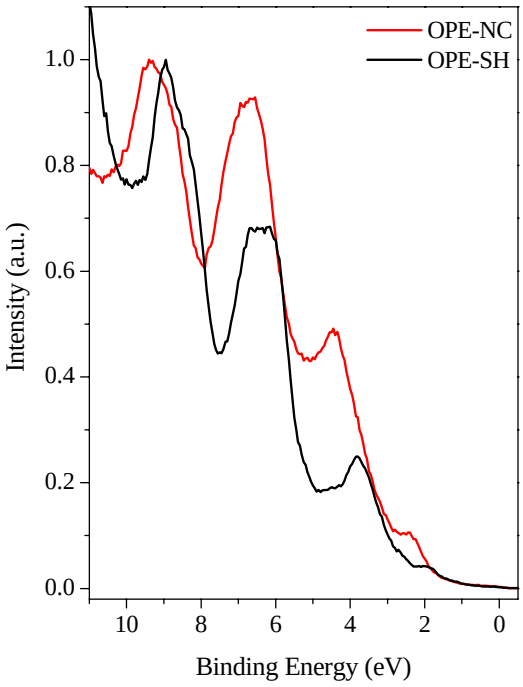


Fig 1: One-photon photoelectron spectra of OPEs adsorbed on Au showing shift in band line-up by varying the linking group from thiol (black line) to isocyanide (red line).

Major Accomplishment: The majority of studies of covalently bound monolayers on metallic surfaces involve thiol-coupling (R-SH) chemistry. Self-assembly of monolayers utilizing thiol chemistry is known to form robust, reproducible monolayers on a variety of metallic surfaces. However, it is important to characterize how the linker group affects the electronic spectra and consequently the band line-up of adsorbed monolayers. Thus, we have undertaken a study of understanding how the band line-up varies as a function of changing the linking chemistry between the molecule and the surface. One-photon photoelectron spectra given in Figure 1 shows that the substitution of the thiol-linker for isocyanide (R-NC) in OPEs adsorbed on Au shifts the position of the occupied and unoccupied states relative to the Fermi level by ~ 0.5 eV. Such a large variation will have a major impact on charge injection in molecular systems. Models for important aspects of the bonding in these two systems to Au have been developed that help explain the observed behavior.

Impact: These results add important insights to the factors controlling band alignment at metal-organic interfaces, a parameter that plays a critical role in potential applications of organic materials in emerging electronic technologies.

Future Studies: We aim to build upon our previous studies of understanding the affect molecular structure and linking-group chemistry have on controlling band line-up in covalently bound molecular systems. Our future work will focus on varying the metal onto which the molecule is adsorbed, as well as alkali metal doping of monolayer films.

Title: Atomic Layer Deposition – Process Models and Metrologies

Authors: *J. E. Maslar (836), W. S. Hurst (836), D. R. Burgess, Jr. (838)*

CSTL Programs: Microelectronics

Vision: Provide measurement standards and advanced measurement methods supporting metrology needs of the semiconductor industry.

Purpose: **D**evelopment of *in situ* metrologies sensitive to ALD chemistry and ALD chemical reaction mechanisms supporting development of ALD process models.

Context: Atomic layer deposition (ALD) is increasingly being utilized as a method of depositing the thin (nanometer-scale), conformal layers required for many microelectronics applications, including high κ gate dielectric layers, diffusion barrier layers, copper seed layers, and DRAM dielectric layers. However, significant developmental issues remain for many of these applications.

One potential solution to some ALD developmental issues is technology computer-aided design (TCAD). TCAD has been identified in the 2003 International Technology Roadmap for Semiconductors as "one of the few enabling methodologies that can reduce development cycle times and costs."[Modeling and Simulation, p. 1] However, many difficult challenges to development of validated, predictive ALD process models that allow prediction of equipment influences on film properties have been identified, including chemical data (e.g., rate constants, cross sections, surface chemistry); reaction mechanisms, and reduced models for complex chemistry. In addition to a lack of quality fundamental physical and chemical data, experimental validation has been identified as a "key difficult challenge across all modeling areas."[Modeling and Simulation, p. 1] Further, with respect to experimental validation, the "major effort required for better model validation is without doubt sensor development." [Modeling and Simulation, p. 15] This project is an attempt to assist in solving some ALD developmental issues by developing validated, predictive process models and associated metrologies for ALD processes.

Accomplishments: This project involves two primary directions: development of *in situ* metrologies sensitive to ALD chemistry and development of ALD chemical reaction mechanisms. These two directions are seen as mutually-supporting. It is expected that experimental results that elucidate ALD chemistry will aid in chemical mechanism development and ultimately in process model validation. Further, it is expected that the most important reaction species will be identified as understanding of a particular ALD reaction improves, thus facilitating the design of improved process metrologies. Ultimately, aspects of both of metrology development and reaction mechanism development will be required to create validated ALD process models. ALD process

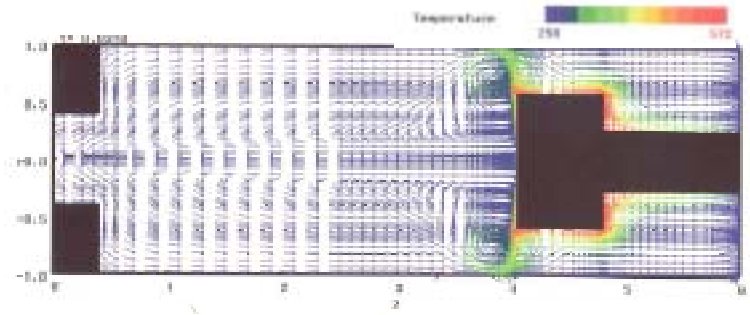


Fig. 1. Numerical simulation of the flow field in the ALD reactor operating at a chamber pressure of 133 Pa (1 Torr), an inlet gas flow rate of 200 standard cubic centimeters per minute and a wafer surface temperature of 572 K.

models would be created by incorporating the chemical reaction mechanisms developed and validated at NIST, then incorporated into commercially available computational fluid dynamics code and then validating the process model under a range of parameters using experimental data collected in the course of this project. Optically accessible ALD reactors have been designed and constructed for *in situ*, high-sensitivity Raman and infrared absorption spectroscopic measurements. Hafnium oxide films will be deposited from tetrakis(dimethylamino) hafnium and water. A two-dimensional numerical model has been developed to simulate the flow of gas and temperature of surfaces in the experimental ALD reactors. Chemical models of HfO_2 and Al_2O_3 ALD process chemistry are being developed and will be incorporated into the two-dimensional numerical reactor model.

Impact: Successful development of in-situ process diagnostics will provide the semiconductor industry with capabilities it current does not have for ALD processes.

Future Directions: During the upcoming year, we plan to use the reactors that were developed during FY2004 to measure the transient species involved in the ALD process. An initial step will be to optimize know ALD recipes to the flow and temperature characteristics of these particular reactors. Then, the process of measuring and model those spectra will begin. Concurrently, we will search for correlations between specific growth steps uncovered by the more sophisticated optical methods with signals from conventional process monitors, such a quartz crystal microbalances and mass spectrometers.

Title: Non-Contact Free Carrier Density Measurements for Compound Semiconductors

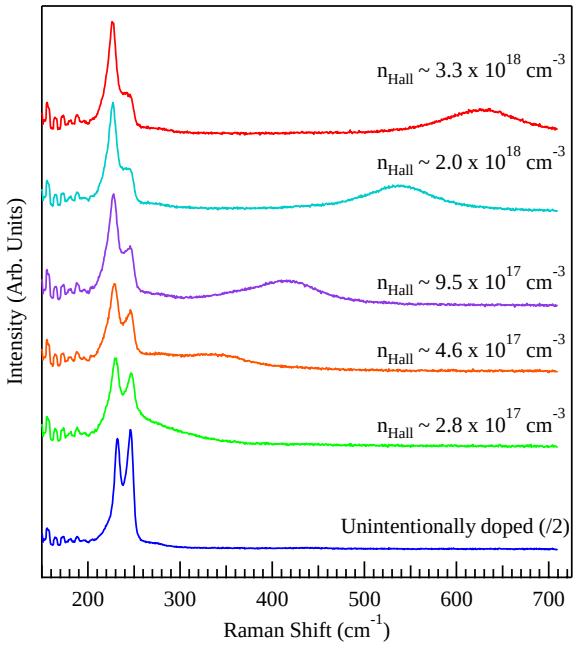
Authors: *J. E. Maslar and W. S. Hurst (836).*

CSTL Program: Microelectronics

Purpose: Develop non-contact measurement methods of electrical carrier, free carrier, and mobility in optoelectronic materials.

Context: Transport of free carriers is central to the operation of all optoelectronic devices and reliable measurement of the carrier properties is critical. Hall or capacitance-voltage measurements are traditionally used to obtain this information, but require electrical contact. This precludes the use of these techniques *in situ* during growth or processing and, typically, even on actual device layers. Raman spectroscopy, as an optical technique that can be used for transport property determination, does not suffer from these limitations. In addition, it is non-destructive, spatially resolved, and can be applied to a specific buried layer, which is sometimes a problem for traditional electrical measurements. A number of issues are central to determining the accuracy and precision of this method, including the semiconductor under investigation, the measurement system parameters, and the Raman spectral model used to fit the measured spectra. NIST is systematically addressing such issues. The results of this investigation should facilitate the utilization of Raman spectroscopy for spatially resolved, off-line characterization as well as process monitoring and control during film growth and subsequent patterning processes.

Accomplishments & Future Directions: Materials with a range of properties suitable for use in a variety of optoelectronic devices operating at different regions of the electromagnetic spectrum are being investigated. The primary focus is on narrow band gap group III-antimonide materials and wide band gap group III-nitride materials. Spectroscopic systems were optimized for each material system after examining thin films of narrow band gap GaSb, GaAsSb, GaInSb, and GaInAsSb and wide band gap GaN, and AlGaN, obtained from various collaborators. Modeling of the Raman spectra from the different materials requires different spectral models that account for the differences in physical properties that make these materials suitable for different applications. Spectral models have been developed for n-type doped GaSb, p-type GaSb, n-type GaInAsSb, and n-type GaN. Efforts are underway to compare the results of the spectral models with electrical measurements to determine the suitability of the respective model.



The Raman spectra of n-type doped GaInAsSb epilayers show a strong dependence on carrier density. The carrier density determined from the Hall effect measurement is indicated. The spectra are offset on the vertical scale for clarity.

Title: Gas Standards Based on Optical Spectroscopies

Author: *J.T. Hodges and P.M. Chu (836); R. Ciurylo (University of Nicolas Copernicus)*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Provide U.S. industry with gas concentration standards based on fundamental properties of the compounds of interest at currently unattainable concentration levels.

Purpose: The goal of this program is to shift the principal realization of traceable gas measurement from one based on consumable artifacts to one based on intrinsic standards. Advances in spectroscopic measurements finally make robust intensity measurements viable for quantitative gas metrology of certain species with an accuracy rivaling and potentially surpassing traditional measurements using artifact standards, particularly for reactive gases.

Context: This program involves the realization and dissemination of primary gas measurement standards based upon quantitative absorption spectroscopy. New applications for gas standards demand high-precision measurements of relatively low concentrations for reactive and non-reactive systems, thus motivating the development of next-generation standards linked to intrinsic molecular properties. Precise spectroscopic measurements are used in conjunction with low-uncertainty methods of sample preparation. This approach yields absolute measurements of ab-

sorption line intensities for a variety of low-molecular weight target analytes such as CH_4, H_2O, NO_x, O_3 and NH_3.

Major Accomplishments: We developed a new approach to CRDS using cw lasers that are frequency locked to frequency-stabilized ring-down cavities. This novel variant of CRDS yields absorption spectra in which the frequency axis and absorption coefficients are directly linked to high-precision frequency counting measurements and measurements of cavity photon decay times, respectively. We demonstrated line intensity measurements of H_2O with a relative precision better than 0.3 % at H_2O mole fractions of 10^{-5}. Automation of the spectrometer was also accomplished this year. The automation method required the development and integration of servo systems to tune the frequency-stabilized reference laser, to frequency lock the ring-down spectrometer to the reference laser, and to lock the probe laser frequency to the ring-down spectrometer, respectively. Measurements of weak overtone spectra of H_2O made with the ring-down spectrometer, shown in the figures, demonstrate the sensitivity and spectral resolution of the instrument.

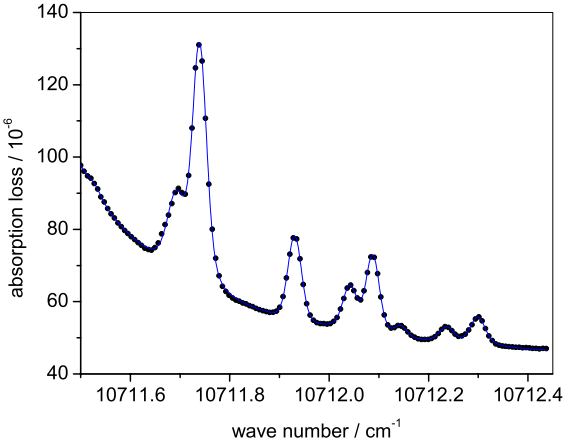


Fig. 1. H_2O survey spectrum measured using frequency-locked cavity ring-down spectrometer

Impact: As an alternative approach to existing primary and secondary gravimetric gas standards, the proposed technique will extend NIST capabilities in gas standards to lower concentrations than are anticipated to be achievable using current methods and to reactive species that are unsuitable for long-term storage in cylinders. Additional advantages to customers include: lower uncertainties, coverage of new species, potentially lower cost for standard mixtures, more flexibility in terms of dilution gases, and the availability of low-uncertainty molecular property data applicable to spectroscopic measurements of gas concentration. Customers include users of NIST standard gas and users of molecular spectroscopy line intensity data. This work is relevant to emissions of toxic industrial compounds and emissions from ground and air transportation systems, air pollution monitoring, metrology of high-purity gases used in manufacturing processes, atmospheric science, defense, health-care diagnostics and homeland security.

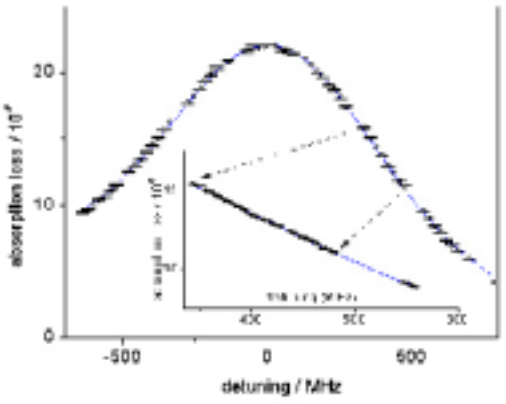


Fig. 2. High-resolution scan of rovibrational H_2O transition obtained with frequency-locked CRDS technique.

Future Plans: We plan to use CRDS to measure spectral line shapes and line intensities of H_2O and CH_4 , and we will pursue applications of CRDS to reactive gases. Comparisons to NIST primary thermodynamic and gravimetric gas standards will be made to maintain links with

existing standards. To address measurement challenges of specific gas mixtures for which component species have overlapping absorption spectra, Fourier-transform spectroscopy will be used to identify optimal wavelength regions where spectral interferences are minimized.

Title: Absorption Coefficient Measurements of Aerosol Particle Agglomerates

Authors: *C. Presser (836), C. Sheng (836), and A. Nazarian (SAIC)*

CSTL Program: Energy and Environmental Technologies

Purpose: Study the feasibility of a new measurement approach for the absorption coefficient of carbon-based aerosol particles at high temperature (up to 1200 K), using controlled laser heating.

Context: Greenhouse effects associated with climate change may be influenced strongly by the chemical and physical properties of aerosol particles in the atmosphere. Currently, the largest uncertainty in predicting the change in Earth's global average temperatures over time is due in part to inadequate knowledge of the optical properties of atmospheric aerosols, such as soot and cloud condensation nuclei. Although a variety of methods are used to measure atmospheric aerosol black carbon mass, those based on thermal-optical analysis (TOA) are widely used in the US. TOA methodology makes critical and untested assumptions about the thermal and optical behavior of PM on a quartz fiber collection substrate, as well as the instrument-produced byproducts of pyrolysis. In response, we have developed a new approach to characterize the optical behavior of soot PM, which combines a laser driven thermal reactor (LDTR), an acoustic levitator, and optical pyrometry, as a well-controlled thermal environment for the non-intrusive determination of optical, thermal-physical, and chemical-kinetic properties.

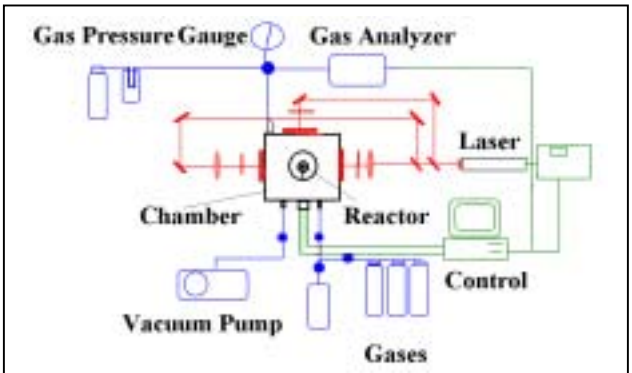


Fig. 1. Schematic of the Laser Driven Thermal Reactor.

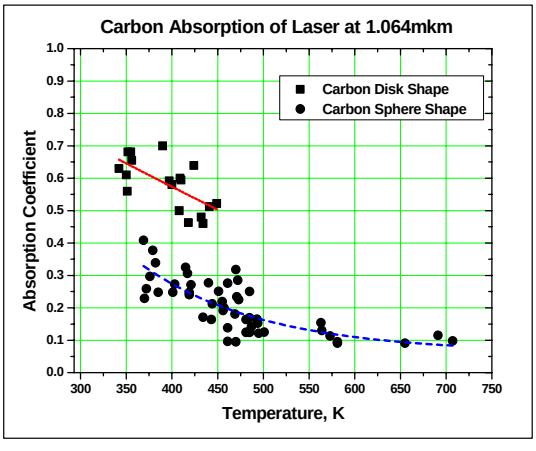


Fig. 2. Variation of the absorption coefficient with sample temperature for the sphere- and disk-shaped carbon.

Major Accomplishments: Measurements were carried out in the LDTR (see Figure 1) to determine the effect of carbon shape and size on its absorption characteristics. This information is important for characterizing particles when their surface is not always spherical and well predicted by theory. Results were obtained for a spherical and disk-shape agglomeration of compacted particles over a range of laser heating temperatures. Figure 2 presents the effect of

heating on the determination of the absorption coefficient. The LDTR was modified to include a chemical sampling and analysis capability. A sampling probe and gas collection arrangement was fabricated and operated by vacuum pressure extraction of gases into a stainless steel accumulator with a septum. The septum allows collection of the gas into syringe, which in turn provides sample for analysis in a gas chromatograph/mass spectrometer (GC/MS). The GC has a capillary column that allows separation for poly-aromatic hydrocarbons (PAH). PAH identification is of interest since they are considered precursors to the formation of soot. The MS (which can scan from 10 to 800 mass/charge ratios) and NIST MS library are used to identify such candidate PAH molecules.

Future Plans: We plan to use this technique to develop a unique database that includes, in addition to soot absorption coefficient, other optical and physical properties for soot, other representative samples of particulate matter, and multiphase and multi-component liquid droplets that are representative of cloud condensation nuclei characteristics. These data will be used to provide input information for climate change models, and to improve the performance of optically based devices used to monitor particulate matter in the environment.

Impact: Determination of the optical absorption characteristics of aerosol particulates with greater accuracy than other existing techniques has excellent potential to improve the performance of thermal-optical analyzers, which are used extensively to characterize aerosol particles that are collected in the atmosphere. In addition, climate models that predict the global average temperature require reliable data on absorption coefficients of particulates, but detailed information on their optical properties is largely unavailable.

Title: Atomic Standard of Pressure

Authors: *M. Moldover, J. Schmidt, E. May (Guest Researcher – Univ. of New South Wales, Australia), Y. Wang (811)*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: **D**evelop a novel primary standard for pressure in the range 0.3 MPa to 5 Mpa based on fundamental physical properties of helium.

Purpose: The determination of pressure $P(\varepsilon,T)$ based upon measuring and calculating the dielectric constant, $\varepsilon(p,T)$, of helium will become the basis for new pressure measurement standards. Ultimately, the uncertainties from impurities, electrical and temperature measurements are expected to be smaller than that of existing pressure standards (piston gages).

Context: Below 300 kPa, the primary pressure standard at NIST is a 3-meter mercury manometer. Above 300 kPa, the pressure standards are commercially manufactured piston-cylinder sets. These sets are complicated artifacts. In operation, the cylinder and piston deform significantly and the piston rotates continuously to insure gas lubrication. Because of these complications, piston-cylinder sets are calibrated using the primary-standard mercury manometer below 300 kPa and their performance is extrapolated to higher pressures using numerical models of the coupled gas flow and elastic distortions. The extrapolation cannot be checked with existing technologies; thus, it is not fully trusted. Furthermore, piston-cylinder sets exhibit poorly understood specie and gas flow dependencies. Should $\varepsilon(p,T)$ of helium become the pressure

standard, it will be possible to test models of piston-cylinder sets and to reduce the uncertainty in the assignment of their effective area.

Progress: Figure 1 is a diagram of an experiment that compared two techniques for measuring $\varepsilon(p,T)$, the dielectric constants of helium and argon, in the ranges 0.1 to 7 MPa and 0 to 50°C. One technique uses cross-capacitors and a capacitance bridge. As sketched in Figure 1, the cross capacitor has four electrodes. In contrast, most capacitors have two electrodes. The extra electrodes compensate for surface contamination (oxides, adsorbed water, or films of oil). The symmetry of the cross capacitor makes it insensitive to microscopic displacements of its electrodes. The second technique for determining $\varepsilon(p,T)$ measures the microwave resonance frequencies of gas-filled quasi-spheroidal cavity, i.e. a cavity with a shape that intentionally differs from a perfect sphere. In Figure 1, quadrants of a perfect sphere have been cut out of the cavity and the asphericity is exaggerated. The microwave resonances of a spherical cavity occur in overlapping multiplets; the resonances of a quasi-spheroidal cavity are separated into easily measured, non-overlapping components.

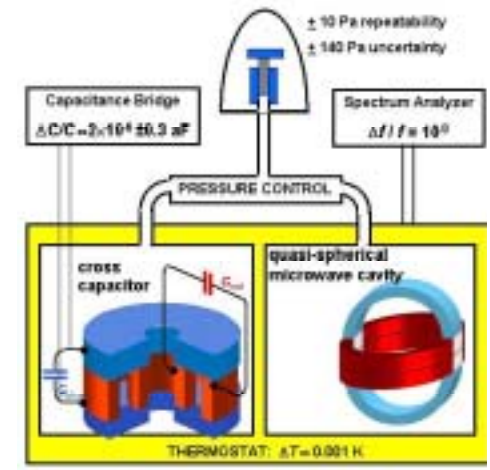


Fig. 1. Comparison experiment. The dielectric constant of either helium or argon is measured simultaneously with a cross capacitor (left) and with a quasi-spherical cavity (right).

Figure 2 shows recent test results. We have measured $\varepsilon(p,50°C)$ of helium and argon. The center panel of Figure 2 shows the differences between $\varepsilon(p,50°C)$ measured using a cross capacitor and $\varepsilon(p,50°C)$ measured using a quasi-spheroidal cavity. The differences have a standard deviation (S.D.) of only 8×10^{-8}. This standard deviation is a factor of 6 smaller than that of our previous report two years ago.

The data in Figure 2 are limited by imperfections of the capacitance bridge, which is the best commercially available. The NIST Small Business Innovative Research Program (SBIR) is supporting efforts to develop a greatly improved capacitance bridge. One vendor has demonstrated that factor-of-10 improvements are feasible and won an SBIR Phase II contract to make a prototype bridge having such improved performance.

Today, measurements of $\varepsilon(p,T)$ made with a quasi-spheroidal cavity have 10 times the resolution of measurements made with the existing capacitance bridge. However, the cavity is not yet an accurate realization of the pressure standard because we do not know the elastic constant k_T that determines how the cavity shrinks under applied pressure. The ultrasonic resonance technique used to measure k_T of solids gave poor results when we applied it to the copper cavity. We shall overcome this problem by constructing new microwave cavities out of copper-platted hard metals.

Impacts: (1) This program will revolutionize the realization of pressure standards. (2) We discovered that gas-filled, quasi-spheroidal cavities are excellent acoustic thermometers. NIST is using them to determine the imperfections of the internationally accepted temperature scale, ITS–90. (3) We used existing cross capacitors to measure $\varepsilon(p,T)$ of the primary constituents of natural gas (CH_4, C_2H_6, C_3H_8, N_2, CO_2, Ar) in the temperature range 0ºC to 50ºC and at pressures up to 7 MPa. These data are more accurate than any previous data; they comprise

reference data for metering natural gas. (4) An improved capacitance bridge will be delivered to NIST. Ultimately, the improve bridge will improve calibrations of capacitors by NIST's Electricity Division.

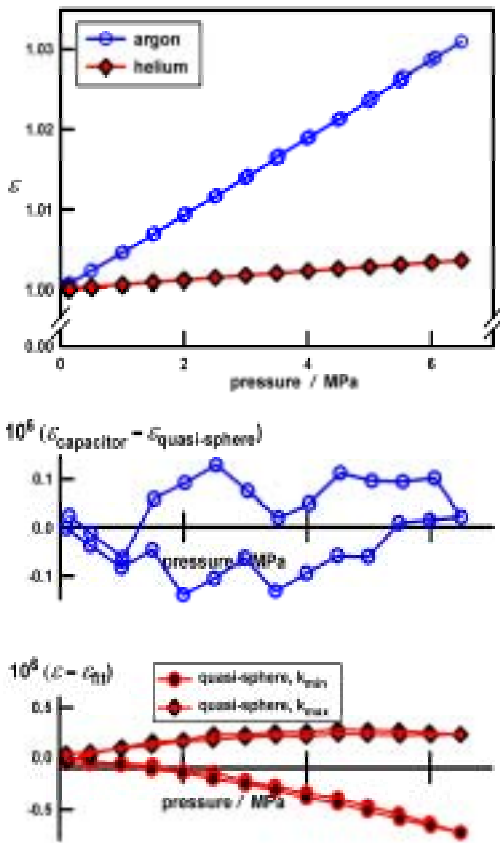


Fig. 2. Deviations of helium measurements relative to theory using extreme values of elastic constant *k*. The curved deviations indicate the 3rd density virial coefficient of helium has an error. Center: Consistent argon results (S.D. = 0.08 ppm) obtained after calibrating the capacitor and the quasi-sphere with helium.

Title: Primary Acoustic Thermometry

Authors: *G. Strouse, D. Ripple, L. Pitre (Guest Researcher – BNM/INM, France), M. R. Moldover*

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Provide fundamental thermodynamic temperature data upon which next generation temperatures scales may be based.

Purpose: To reduce (1) the uncertainty in the thermodynamic temperature by a factor of 3-8 from 77 K to 900 K, using speed-of-sound measurements in either low density helium or argon gas as a primary standard and (2) the uncertainty of the high-temperature fixed points (e.g. tin point, zinc point) and radiometry tied to these fixed points, and (3) to investigate the feasibility of replacing an interpolating gas thermometer with an acoustic thermometer in the range 3 K to 24.6 K.

Context: The most accurate determinations of thermo-dynamic temperature above 700 K use relative radiance measurements referenced to a black body operated near 700 K. The thermodynamic temperature of the black body is known from NIST constant volume gas thermometry (CVGT). Unfortunately, two NIST CVGT measurements differ from each other for reasons that are not understood. The difference leads to an estimated uncertainty of 13 mK in temperatures near 700 K and 50 mK in temperatures near the gold point (1337.33 K). Similar inconsistencies in the determination of thermodynamic temperature occur below 273.16 K, reaching ±0.005 % at 90 K and below.

In the range 3 K to 24.6 K, NIST fulfills its commitment to support the International Temperature Scale (ITS-90) by maintaining an interpolating gas thermometer as a primary standard. However, this instrument is difficult to use. It is possible that an acoustic thermometer would be easier to use and would yield more accurate results.

Approach: NIST has developed spherical and quasi-spherical, noble-gas-filled cavities that function as acoustic thermometers. We measure the frequencies of both the acoustic and the microwave modes in the cavities while the cavities are enclosed by a high-performance thermostat. The data determine the speed of sound in the gas from which the Kelvin thermodynamic temperature T is deduced. Simultaneously, we measure the cavity-wall temperature with standard platinum resistance thermometers calibrated on the ITS-90 to determine $T - T_{90}$, the deduced of temperatures on the ITS-90 from the thermodynamic temperature. For acoustic thermometry, the measured quantities are frequencies and temperatures. For CVGT, the measured quantities are pressures and temperatures; thus, the two approaches to thermometry have different systematic effects.

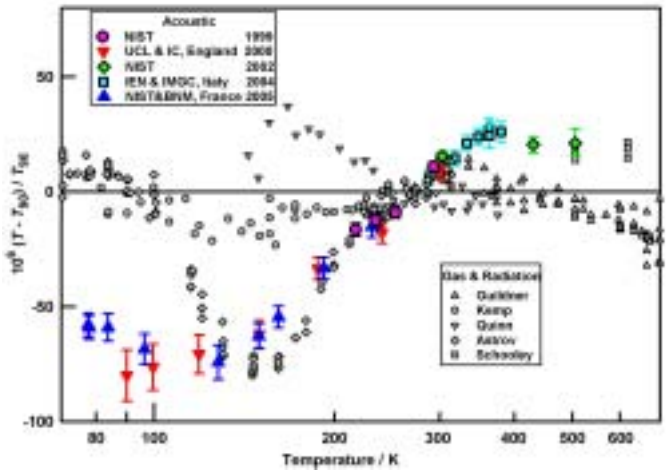


Fig. 1. Fractional deviations from the ITS-90 in parts per million. The colored symbols represent acoustic thermometry; the black symbols represent gas and radiation thermometry used to develop the ITS-90.

Results and Plans: Microwave and acoustic data spanning the temperature interval 85 K to 505 K have been acquired using two different resonators (one copper and one steel) and two different gases (helium and argon). In the limited region of overlap (217 K to 273 K), the results from the two resonators agree within combined uncertainties and determine ($T - T_{90}$) with a standard uncertainty of 0.6 mK. Figure 1 displays these data and acoustic thermometry data from other laboratories, as well as the data that was used to establish the ITS-90.

The present work has resolved the discrepancy in NIST's CVGT. In particular the acoustic measurement at 505 K agrees with the CVGT of Schooley and is inconsistent with the CVGT of Guildner. The high-temperature (steel) acoustic thermometer has been rebuilt in FY04 to give better resolved acoustic resonances and improved thermal performance, and this work will be extended to 700 K, or higher.

The NIST approach to acoustic thermometry has been adopted by independent groups working in England and in Italy. A Guest Researcher from BNM/INM of France, working at NIST, (Laurent Pitre) will continue acoustic thermometry below 77 K when he returns to France in 2005. We have indications that acoustic thermometry will work in the range of the interpolating gas thermometer (3 K to 24.6 K) and will pursue these measurements to investigate the feasibility of such a replacement scale realization method.

Impact: Figure 1 demonstrates that the acoustic thermometry results from laboratories in various countries have a better mutual consistency than the earlier results (using other techniques) that were used to establish the ITS-90. Thus, a consensus is growing concerning the imperfections of the ITS-90. The acoustic thermometry results will be incorporated into a new temperature scale that will have errors that are a factor of 5 to 8 smaller than the errors in the ITS-90.

Title: Thermophysical Properties of Gases used in Semiconductor Processing
Authors: *J. J. Hurly, K.A. Gillis, and M.R. Moldover*

CSTL Program: Microelectronics

Purpose: CSTL continues to respond to the expressed need of the US semiconductor industries for gas property data by measuring the thermophysical properties of semiconductor process gases.

Context: These measurements exploit novel, accurate, NIST-developed acoustic techniques. The measured properties include the speed-of-sound, ideal-gas heat-capacity, density (equation of state), viscosity, and thermal conductivity. Representatives of the semiconductor industry have identified the highest priority process gases, "surrogate" gases, and the binary mixtures of process and carrier gases as well as targets for accuracy required to model manufacturing process Specific areas that will benefit from this work are chemical vapor deposition (CVD) processes and the calibration of mass flow controllers (MFCs) using surrogate gases. (See Figure 1.) NIST disseminates them via the internet at the URL http://properties.nist.gov/semiprop (Figure 2) as results are acquired. The database includes the heat capacity at constant pressure, thermal conductivity, viscosity, and virial coefficients $B(T)$ and C(T) that determine the pressure-density-temperature relation. gaseous mixtures of process

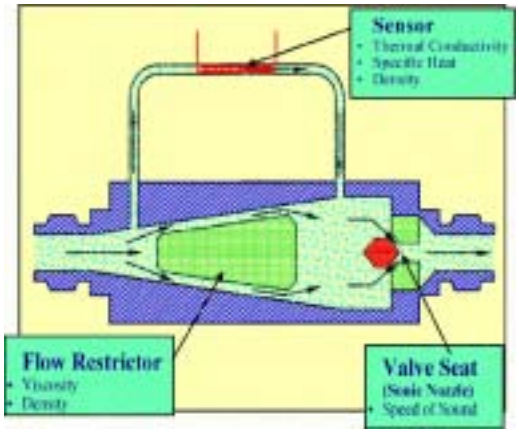


Fig. 1. Components of a generic mass flow controller (MFC) and the thermophysical properties required to model them.

Accomplishments and Impact: The Greenspan viscometer was installed in a facility for handling hazardous gases. The viscosity was measured in 12 process and 'surrogate' gases. (See Table 1.)


Tungsten Hexafluoride

WF_6

M.W. [1]	N.B.P. [2]	T.P. [2]
297.84	290.25 K	275.0 K

P_c [3]	T_c [3]	V_c [3]
4.57 MPa	452.7 K	0.1 $m^3/kmol$

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T K	$C_p^0(T)/R$	Vapor Pressure MPa	$B(T)$ $cm^3 mol^{-1}$	dB/dT $cm^3 mol^{-1} T^{-1}$	$C(T)$ $cm^6 mol^{-2}$	dC/dT $cm^6 mol^{-2} T^{-1}$	λ (mW/(m·K))	η μPa·s
Estimated Uncertainty	1%	1%	Our densities are calculated to better than 0.1% over the temperature and pressure ranges of the reference.				10%	10%
Reference	[4]	[6]	[5]	[5]	[5]	[5]	[5]	[5]
205	11.84	0.19	-2001.6	5951.2	-4658932	47121716	-	-
210	12.00	0.34	-1864.5	5441.0	-3653771	36754361	-	-
215	12.16	0.58	-1741.8	4994.1	-2884907	28904191	5.2	14.17
220	12.32	0.95	-1631.6	4600.8	-2291407	22949084	5.4	14.41
225	12.48	1.53	-1532.2	4252.9	-1829413	18345717	5.6	14.64

Fig. 12. Sample Web Page from database located at the URL http://properties.nist.gov/semiprop/

By the end of FY04, we used a Greenspan acoustic viscometer to measure the viscosity of 12 gases under the conditions listed in Table 1. The acoustic viscometer also determines the speed of sound in the test gas. As in the past, speed of sound was used to determine the ideal-gas heat-capacity to within 0.1 % and virial coefficients that reflect each gas's non-ideality.

ideality. From the virial coefficients, we developed an equation of state that predicts the gas's densities to within 0.1 %.

The results of this research have been disseminated through publications in professional journals and by a series of talks at professional meetings. During FY04, three new publications were published in archival journals. Dr. John Hurly is the Technical Editor of the Gases and Facilities Standards Committee of SEMI (Semiconductor Equipment and Materials International). This year, the committee gave Hurly an award for his "outstanding contributions" to the committee's work.

Future Plans: In FY05, we shall install a new monel spherical resonator and measure the speed of sound in two semiconductor process gases such as HF and SiF_4 to determine the 'best in the world' equation of state for each gas.

We will measure the viscosity of four hazardous process gases such as: SiF_4, C_4F_8, CO, and CO_2. The NIST results will decrease the uncertainty of the viscosity from an estimated 10 % to approximately 0.5 %.

Table1. Gases and Conditions for Viscosity Data.

Gas	Temperature Range (K)	Maximum Pressure, MPa
He	**298**	**3.3**
Ar	**200 - 375**	**3.3**
N_2	**298**	**3.3**
C_3H_8	**225 - 375**	**0.9**
SF_6	**298**	**1.8**
CF_4	**200 - 375**	**3.3**
C_2F_6	**225 - 375**	**2.8**
N_2O	**225 - 375**	**3.4**
NF_3	**225 - 375**	**3.4**
BCl_3	**300 - 400**	**1.3**
Cl_2	**280 - 400**	**3.2**
HBr	**225 - 400**	**3.3**

We will continue to disseminate our experimental results through publication of quality manuscripts, frequently updating the online database, and continued interactions with the semiconductor standards community.

Title: In-situ Monitoring of Ion Bombardment Energies in Plasma Etchers for Improved Wafer Yield and Throughput

Author: *Mark Sobolewski*

CSTL Program: Microelectronics

Purpose: Develop non-intrusive monitoring techniques for ion energy distributions in semiconductor manufacturing tools.

Context: During plasma etching processes used by the semiconductor industry, silicon wafers are bombarded by reactive chemical species and energetic ions, resulting in selective removal of material from exposed areas of the wafer. The energy of ions striking the wafer surface plays an important role in determining the etching rate, the profile of etched features, and the extent of plasma-induced damage. To obtain the best results, the kinetic energy of ions must be carefully optimized and controlled. Unfortunately, control of ion energy in industrial reactors is difficult because of the lack of reliable methods for *in situ* monitoring. Traditional methods for measuring ion energy, which require that an ion energy analyzer be inserted into the plasma, are not compatible with industrial reactors. Typically, an analyzer will not survive very long when exposed to industrial plasmas, and it may cause contamination of the wafers being processed. Also, analyzers do not measure the ion energy at the most relevant location, the wafer surface.

Major Accomplishments: A method for *noninvasive* monitoring of ion kinetic energy has been developed and demonstrated in CSTL's Process Measurements Division. It does not require that anything be inserted into the reactor. Instead it relies on measurements of the applied radio-frequency current and voltage, which are easily measured outside the reactor without any perturbation to the plasma or the process. These measurements are analyzed using electrical models of the plasma to determine the ion flux and ion energy distribution at the wafer surface.

The method has been validated by comparisons with invasive ion energy measurements, and has recently been used to monitor drift in an inductively coupled plasma reactor. Over time, an electrically conductive layer builds up on insulating surfaces inside the reactor. This layer interferes with the operation of the inductive plasma source, causing a long-term downward drift in plasma density and ion flux. These changes in turn produce drifts in ion energy, which were monitored using the noninvasive technique. Depending on conditions, ion energies can either increase or decrease. In one experiment a change larger than 100 electron volts was detected. Such large changes in ion energy would certainly have deleterious effects on wafers being processed.

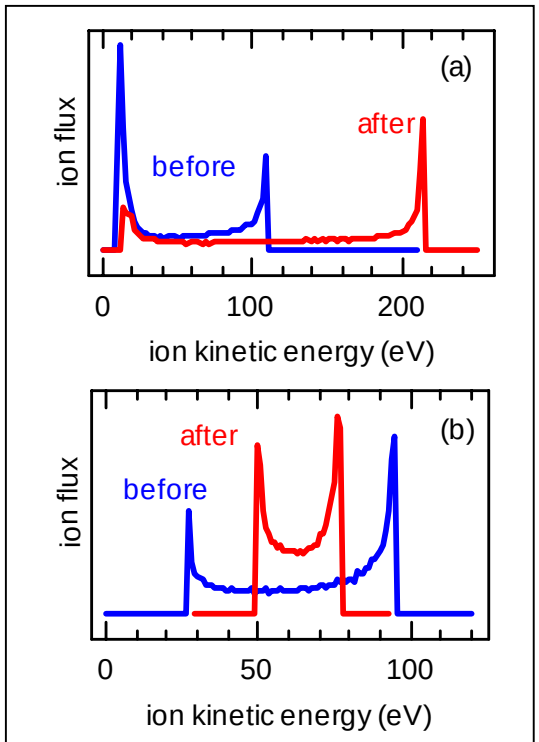

Fig. 2. Ar^+ ion energy distributions obtained from noninvasive electrical measurements before (blue) and after (red) deposition of a conductive film on the inductive source window, for 10 mTorr argon plasmas at 100 W inductive source power. (a) constant bias power at 1.0 MHz, and (b) constant bias voltage at 10 MHz.

Impact: The non-invasive monitoring technique now enables early detection of ion energy drift so that response strategies can be implemented to prevent costly wafer damage. The technique has also provided a better understanding of drift mechanisms that could further help process technologists and equipment engineers to minimize and eventually eliminate ion energy drift.