Process Measurements Division - Table of Contents

Process Measurements Division

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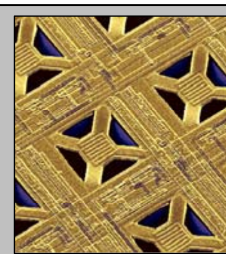


Process Measurements

J. Whetstone, Chief

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

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 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.

Organizational and Project Structure:

The Division has 69 full-time staff members, organized in 6 groups, representing a range of technical competencies and is organized to establish, strengthen and extend them. 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 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.

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]
- Particulate Standards and Measurements [07, 837]

Molecular Electronics Project – 836.00

- Two Photon Photoelectron Spectroscopy
- Molecular Self Assembly

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

- 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, Opto-electronics, 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.

Project and Program Areas:

The Division's measurement science research and standards realization and dissemination activities generate accomplishments in several of CSTL's 14 program areas. The Division has responsibilities for establishing, enhancing, and disseminating national measurement standards; summarized in the first four project descriptions given below. A broad competency in calibration metrology is a strong contributor to meeting these responsibilities. We provide traceability of measuring instruments for U.S. industry and government agencies primarily by provision of instrument calibration services and special tests. Where traceability of measurements is more effectively provided to customers through Standard Reference Materials and Data, we utilize those mechanisms.

Demonstration the level of equivalence of U.S. national measurement standards with those of other nations continues to be a significant effort. Division participation in comparison efforts are focused on key comparison activities organized by the Comité International des Poid et Mesures (CIPM), by the CIPM's consultative committees and by Regional Metrology Organizations. NIST is a leading member of the Sistema Interamericano Metrologia (SIM – the Inter-American Metrology System). These efforts occur in several Groups and support CSTL's International Measurement Standards program. Over the past several years, a substantial number of comparisons have been completed temperature and pressure and vacuum standards, such that few needs remain at the CIPM level. New efforts at a reduced scale are primarily 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.

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
- Improve temperature measurements and standards

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

National measurement standards for humidity are developed to extend their range and reduce measurement uncertainty and are disseminated through calibration services. Research efforts and standards activities focus on:

- Providing access to national measurement standards through the provision of measurement services available to industry, government, and the public;
- 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 ng/g) levels. The Division is disseminating through instrument calibration services and special tests. We are developing rapid, low cost methods for calibration of permeation tube generators to provide semiconductor manufacturers, gas suppliers, and instrument makers with standards of improved accuracy to facilitate improvements in process control.

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.

Research activities improve the realization of both primary and transfer standards to anticipate future measurement and standards needs of industry. Research efforts improve efficiency and accuracy of calibration services, both those supplied by NIST and by NIST's customers. Examples of current research efforts include projects to develop:

- An intrinsic primary pressure standard based on the dielectric constant of helium calculated from first principles;
- Next-generation vacuum gauging technology to unstable ionization gauges;
- Improved low-range flow rate standards; and
- A database of out-gassing rates from stainless steels to enable construction of chambers to achieve extreme vacuum levels.

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 of chemical warfare agents. Nano-phase, doped sensing oxides have been shown to produce high sensitivities without the fouling effects that are often observed on metal 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. These 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.

Current research is focused on a model, prototypical BioMEMS device and reaction: the melting of DNA on μHP devices. The heat producing and temperature measurement capabilities of μHPs hold great promise for monitoring and detecting biological reactions in MEMS device formats.

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 dielectric constant values lower than that of currently used silicon dioxide. 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 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 electronic 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 microgravity. 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 microgravity.

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.

Particulate Measurements and Standards

A major coordinated effort across Federal and State agencies is underway to improve the understanding of airborne particulate matter (PM) and its effects upon human health. 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 following CSTL programs:

- 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

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 NIST standards activities and end users of measurements. The Division disseminates U.S. national measurements standards and develops improved methods of realization of national measurement standards. Most of these efforts occur in the four standards-oriented projects of the Division: Fluid Flow, Temperature, Pressure and Vacuum, and Humidity. 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.

<u>Calibration Services</u>

Although Standard Reference Materials (SRMs) and Data (SRDs) are utilized in some cases to disseminate measurements standards, 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 2000 thru 2003. Substantial yearly fluctuations in calibration requests are often encountered. The total calibration workload in FY 03 consisted of 640 instruments. The total number of calibration

Quality System Supporting Calibrations

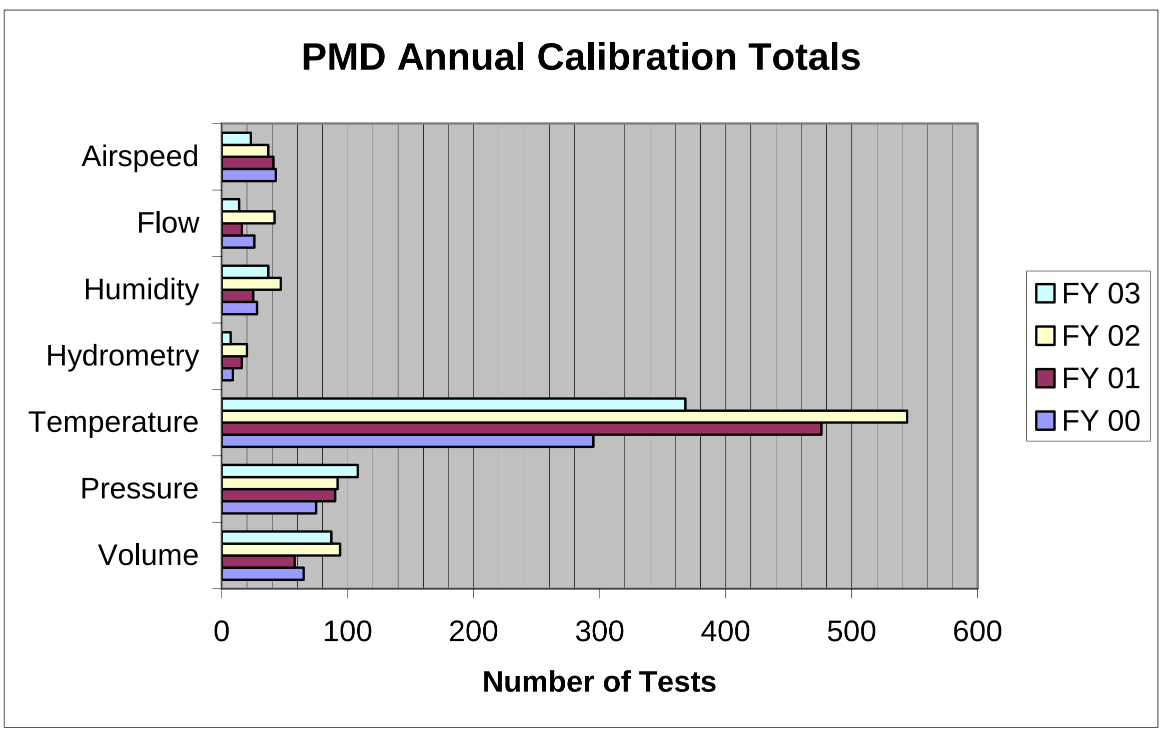
NIST established its policy on quality systems support measurement services in FY03 to support NIST's self-declaration of its quality systems supporting Calibration and Measurement Certificates in compliance with the CIPM Mutual Recognition Arrangement. The NIST-level quality manual was completed and has now been adopted for use. Each Laboratory/Division having measurement standards responsibilities must have a fully documented quality system in place that conforms to the requirements of ISO 17025. The approach is multi-tiered and modular. To self-declare the assessment of its quality system NIST has put an assessment system in place that is:

- Internal to NIST,
- The same for all Labs, Divisions, and Services,
- As independent and objective as possible, and
- Focused on quality management as opposed to technical competence, which is presumed.

Full operation of the NIST Quality System has two primary phases that will result in completing:

- Initial documentation assessments by December 31, 2003
- Full assessments by December 31, 2004

The Process Measurements Division completed an internal assessment/audit of the documentation portion of its quality system in FY03. Assessment teams were drawn from NIST staff from the Division, other NIST Divisions having standards responsibilities, and and staff from NIST's Laboratory Accreditation Group. All Division Staff directly involved in calibration and standards realizations participated in the audit as both auditors and as those with calibration service responsibilities. This team was organized to review PMD's Quality Manuals and to assess selected samples taken from each calibration service offered by the Division



Process Measurements Division Instrument Calibrations for Fiscal Years 2000 through 2003

Assessment results indicated that PMD's Quality Manuals are basically equivalent to ISO 17025 Requirements for the Competence of Testing and Calibration Laboratories and its calibration services only needed relatively minor upgrades to comply with the NIST-wide objectives of 17025 equivalency by December 2003. PMD's calibration Groups have specific plans in place to be compatible with the ISO 17025 format in 2004.

Improved Realization of Measurement Standards

Research efforts associated with our standards activities seek to improve realizations of our national primary standards that are the basis for providing measurement services to our customers. A number of accomplishments in FY02 are having significant impact on the ability of the Division to disseminate these standards and on their uncertainty.

In the Fluid Flow Project, an effort to significantly reduce the measurement uncertainty for low to moderate range flow standards for hydrocarbon liquids has made significant progress with the characterization of a new volumetric flow standard. An uncertainty analysis has been completed and demonstrated near the 0.02% level for flows ranging from (0.1 to 3 gallons/minute). This is an approximately 10 times improvement over our current gravimetric method. Characterization is expected to be completed in the 1st quarter of FY 04 with calibration services based on this device planned for February 2004.

Refurbishment of the water flow rate measurement facility is scheduled for completion in mid-FY03. Research on methods to reduce this gravimetrically based system's measurement uncertainty has resulted in development to substantially reduce diverter valve effects on the uncertainty. Several variations in the general approach have been developed conceptually and one was chosen for testing and implementation. Initial testing indicates substantial reduction in diverter error component contribution. This design has been incorporated into the refurbished facility.

The development of intrinsic pressure standards in the range 0.3 MPa to 5 MPa is a long-term Division goal that is based on both the measurement and first principles calculation of the dielectric constant $\varepsilon(p,T)$ of helium. The extraordinary improving accuracy of quantum mechanics-based calculations continues to improve. This new approach to primary standards for pressure will permit the determination of the pressure $p(\varepsilon,T)$ from electrical and temperature measurements to have a smaller uncertainty than the determination of pressure using existing methods to realize standards (piston gages), which are thought to be reaching the practical limits of their realization. Measurement completed in FY 03 had relative uncertainties of $5\mathrm{x}10^{-5}$. Efforts continue to improve this performance by the factor of ten necessary to exceed current pressure standard uncertainty.

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 meaurement standards. In addition, coordination of similar efforts with Regional Metrology Organization (RMO) such as the Sistema Interamericano Metrologia (SIM), which includes the countries in the Americas, extend the comparison efforts to as many 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.

Since 1999 the Division systematically compared U.S. national measurement standards to establish degrees of equivalence of U.S. national measurement standard with those of other NMIs. Additionally, CMC capabilities reflecting our calibration services have been placed in the BIPM database developed for their publication. These international activities add value to NIST calibration services, particularly for our customers involved in international trade. These MRA-related activities guarantee recognition of U.S. standards by U.S. trading partners.

NMIs signatory to the MRA are required to use a quality management system to ensure the continued validity of the claims of calibration and measurement certificates remain valid. NIST, CSTL, and Division efforts to develop such a system were described above.

The Process Measurements Division has significant participation in the CC's for Temperature (CCT) and Mass (CCM). We have lead or participated in many KCs in the past several years. In thermometry, these efforts have resulted in establishing equivalence levels over the ITS-90 range from 14 K to 1235 K. KCs organized by the CCM include Division activities in both the pressure and vacuum and the flow project areas. In the pressure and vacuum project the Division leads or participates in KCs that cover the pressure range $3x10^{-6}$ Pa to 500 MPa. NIST has piloted three CCM Key Comparisons in the last several years, completing two in FY02 that demonstrated general equivalence among the participants, revealed no systematic bias between alternative realizations of the Pascal, were the only CCM KCs completed on schedule, and set the standard for the manner in which KCs should be conducted. A summary of these activities and accomplishments is given in the technical reports following this overview.

G. E. Mattingly continues to chair the CCM's Working Group for Fluid Flow (WGFF). Through FY 03, the WGFF has progressed applying its strategy to produce Key Comparisons (KCs) in seven different flow measurement areas: water, hydrocarbon liquids, low-pressure air, high-pressure and high-flow natural gas, high pressure nitrogen or air, air speed, and liquid volume. In each of the seven flow areas, different NMIs have accepted the responsibility to produce transfer standards and the test procedures needed to compare the respective flow standards of the participating NMIs. One of these-the Korean Research Institute for Standards and Science (KRISS) has completed this work in water flow and with approvals from the CCM, has officially started the first WGFF KC. This KRISS program is expected to set precedents that should advance the state-of-the-art in conducting all future flow laboratory comparisons. The WGFF chair continues to work closely with the NIST Statistical Engineering Division (SED) to develop sound, statistically based test procedure designs and supporting analysis methods applicable to all KCs. Additionally, the WGFF chair works with the NIST/SED to assess the metrological linkage techniques that will be required to connect the results of the KCs to the associated Regional Metrology Organization (RMO) tests that will follow the KCs to metrologically link all of the participating NMIs.

NIST will pilot the KC for the low-pressure gas flow. Recent advances in U.S. standards and procedures (see accompanying technical report) are expected to materially improve the performance-level of this KC. Characterization of the transfer package will begin in FY04.

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 below the µg/g 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 is currently underway. The results of this effort will be published in early FY 04.

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 last years efforts to use localized heating created by a micro-hotplate, a self-heating MEMS structure, in a cold CVD system to selectively deposit carbon on the surface of the device, zinc oxide nanowire structures were shown to be deposited on contact electrode surfaces. This is an initial step toward developing electrical contacts for nanolasers based on nanowire systems. Future efforts will investigate other optically active materials, e.g., gallium nitride-based nanowires which have potential to emit in the near UV and blue regions of the spectrum.

In the Micro-Fluidics and Bio-MEMS project research efforts have resulted in a number of accomplishments in FY 03 addressing methods to concentrate and detect biological analytes in micro-fluidic systems. In FY 02 a new technique for analyte concentration in microchannels, Thermal Gradient Focusing (TGF), was demonstrated. Further work in FY 03 resulted in invention of the first electrokinetic focusing method, Micellar Affinity Gradient Focusing (MAGF), that provides the ability to concentrate and separate analytes based upon properties other than electrophoretic mobility or isoelectric point. A patent application for MAGF has been filed. This work is described in more detail in one of the technical reports following this overview. Additional work with TGF this year has resulted in the demonstration of fast, simple nucleic acid assays that are easily incorporated in capillary or lab-on-a-chip formats. These efforts are directed at new measurement technology development with application in the health and medical products area.

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. Response testing of both simulants and agents have been conducted. Individual micro-sensors were tuned for specific agents by incorporating metal oxide films of different composition in arrays, and by selecting different fixed and time-varying temperature programs. Simulant material tests at NIST of appropriate device prototypes followed by testing at a surety laboratory investigating sensor array sensitivity, reproducibility, and stability. Sensitivity levels well below toxicity levels were demonstrated.

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. A new electrical measurement method is being developed that is sensitive to the wetting properties of surfaces and the chemical composition of liquids. In this technique, thin film micro-heaters (μHs) immersed in a fluid are heated using a voltage pulse of 2-10 microseconds in length. Using the μH as a resistance thermometer, micro-boiling of the liquid, or bubble nucleation, is detected as a change in the heater temperature during the voltage pulse due to the difference in the thermal conductivity of the vapor versus that of the liquid. Complex micro-machined devices are not required; the measurement can be performed with structures as simple as a thin metal line on a substrate. The measurement is novel, easy to perform, and fast. The technique has potential for the detection of surface binding events such as those found in gene and protein chips.

Awards in FY 2003:

Will complete when I return. 11/8/03

Molecular Electronics Metrology

Authors: J. D Batteas,* J.C. Garno,* C.A. Gonzalez[†], C.A. Hacker, [¤] L.J. Richter,* S. W. Robey,* C. D. Zangmeister,[‡] and R. D. van Zee[‡] ([¤]Div 812 [‡]Div 836, *Div 837, [†]Div 838)

CSTL Program: Technologies for Future Measurements & Standards

Scientific Objectives. Molecular Electronics (“moletronics”) is a field that many predict will have important technological impacts on the computational and communication systems of the future. In these systems, molecules perform the functions of electronic components. Our objectives are to characterize the structural properties of, and the conduction mechanisms through, molecules and to develop methods that reliably and reproducibly measure the electrical properties of molecular ensembles in test structures.

The drive to increase electronic device performance, with the associated push to ever smaller device dimensions, has lead industry observers to conclude that silicon-based technology will reach a point of diminishing gains in the near future. This, in turn, has generated interest in alternative technologies based, for instance, on single-electron devices and molecular components. It is hoped that the tremendous flexibility available with organic synthetic chemistry and self-assembly techniques can be harnessed to produce non-linear devices analogous to silicon-based diodes and transistors, but comprised of single or small numbers of molecules. The CSTL team of researchers in molecular electronics is integrating a range of techniques that will provide key information on electronic structure and electron transport in candidate molecular electronic systems. The methodologies being employed include two-photon photoemission, which accesses unoccupied electronic levels and tracks electron relaxation effects, scanned probed microscopies, which can characterize electron transport down to the single molecule level and afford means of manipulating matter on the nanometer scale, as well as theoretical modeling of electronic states and transport properties to better elucidate the mechanisms involved in such transport function.

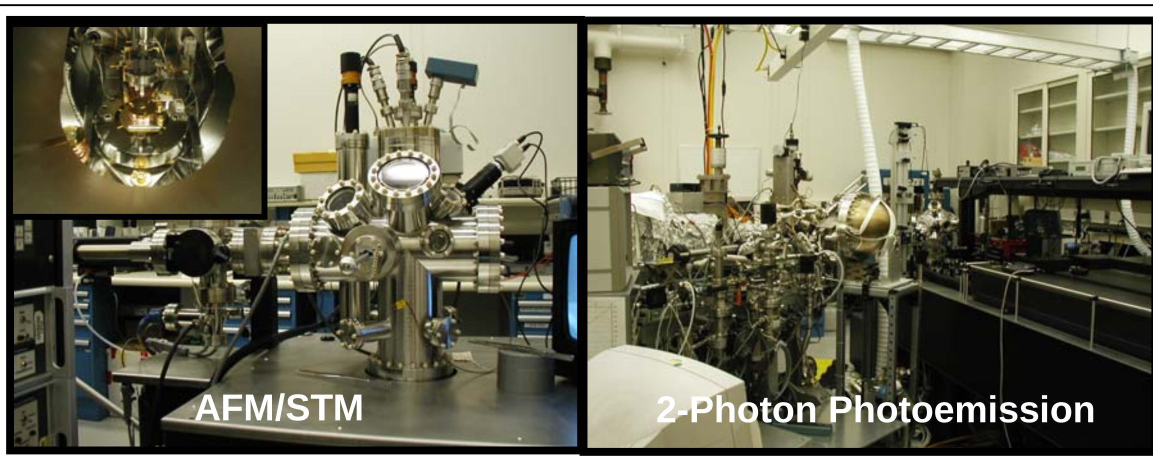


Fig. 1. Left, Atomic-Force/Scanned-Tunneling Microscope used for film characterization studies. Right, Photoemission system used to study molecular electronic structure.

Purpose: This work will develop measurement techniques and expertise necessary to understand electronic structure and transport found in molecular systems comprised of organic thin films and small ensembles. The overall goal is to reliably provide experimental details which, when coupled with theoretical input, will help to elucidate the physical mechanisms that produce device function in molecular based systems. This work is also aimed at providing the requisite measurement protocols for such systems.

Major Accomplishments: *Theoretical Studies of Electron Transport in Molecular Wires*. We have continued our study of the possible mechanisms governing electron transport in molecular wires. Particular attention has been focused to the electrostatics at the molecule-metal interface, which has been found to affect significantly the transport properties of the system. In order to properly describe the electrostatics at the interface, a novel algorithm has been developed that efficiently computes the electrostatic potential by solving the Poisson equation at each cycle of the self-consistent field iteration based on *ab initio* electronic structure calculations. A result of this calculation is shown in Figure 2. This algorithm has been used to study the possible sources that lead to asymmetric current-voltage (I-V) curves in atomic wires as well as in a series of organic thiolates connected to gold electrodes. In order to develop efficient and robust models to gather a qualitative picture of electron conductance through molecular bridges, a simple algorithm to compute the first-order expansion of the system's Green function projected only onto fragments of the isolated molecule (no electrodes are included) has been implemented. This simple model, called the Green Function Condensed-to-Fragments model (GFCF) was found to be very useful in studying electronic transport properties of molecular bridges where the contact to the electrodes does not seem to play an important role in determining the shape of I-V curve. This approach has been used to compute I-V characteristics of the molecule 2'amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiolate (NH_2-NO_2-OPE), found to exhibit "negative-differential resistance" (NDR) behavior at 60 K. The results of the calculations are in good agreement with the experimental I-V curves. Calculations based on the same model predicted that the fluorinated derivative 4,4'-di(ethynylphenyl)-2'-fluoro-1-benzenethiolate (F-OPE) was also a good candidate for NDR behavior. Chemists in the Nanotechnology Group at Kraft Foods worked on the synthesis of the molecule and very recently, scientists in NIST's Surface and Microanalysis Sciences Division (837), have made I-V measurements that qualitatively agree with the predictions of this model. This is the first time that a theoretical prediction of the behavior of molecular bridges upon electrification has prompted experimental work leading to its validation. These results indicate the potential of theoretical tools in the rational design of electronic devices at the nano-scale.

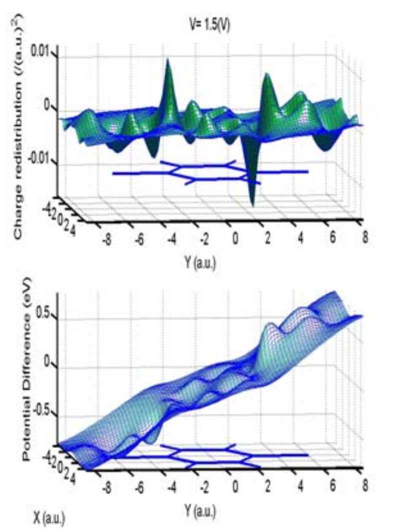


Fig 2. Charge Distribution and Electrostatic Potential profiles for benzene di-thiolate attached to gold electrodes.

SPM Directed Device Fabrication. Precisely engineered nanostructures provide a means for the exploration of chemical reactions under spatially well-defined and controlled environments. Although not yet practical for high throughput applications and manufacturing, scanning probe lithography studies provide fundamental information on tip-surface interactions, structures, and properties at the level of nanometers. Under the support of ATP, nanometer-sized patterns of copper were constructed at dimensions ranging from 100 nm to 400 nm via AFM-based lithography (Cf. Figure 3). The writing density and

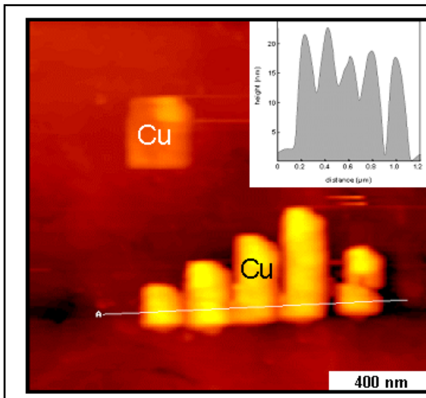


Fig 3. Pattterned Cu contacts on the SAM surface. Patterns range from 150 nm to 400 nm and are ≈20 nm thick.

size of the patterns affect copper growth. Varying solution chemistry parameters, such as the immersion intervals and the concentration of metal salts, can control pattern sizes**.** Copper grows beyond the edges of the pattern boundaries. An effective resist was found using mercaptoundecanol, with very high selectivity observed, even at the nanometer scale. Longer chain length alcohols (C_{11} vs. C_6) were more effective as resists. Preliminary results using silanized tip coatings are promising for inhibiting copper deposition on AFM tips during *in situ* experiments. Future work will investigate charge transport with copper overlayers on SAMS using conductive probe AFM measurements at a metal-molecule-metal interface.

Orientational Effects on Electron Tunneling in Dodecanethiol. Obtaining a detailed understanding of electronic transport properties in molecules requires the ability to correlate structure and transport mechanisms. Here we are utilizing dodecanethiol as a "standard" test molecule to provide reference I-V measurements. This molecule affords a means of probing the impact of molecular orientation on tunneling behavior. Self-assembled monolayers of dodecanethiol have been prepared with regions of densely packed molecules whose molecular axis is oriented $\approx 30^{\circ}$ from the surface normal right next to regions of lower density molecules which are arranged with the molecular axis parallel to the surface. Asymmetry in the tunneling I-V curves show that, in the case of the standing up phase, the tunneling behavior is rectified by the asymmetry of the transport junctions, while in the laying down molecule, this asymmetry is almost completely removed (Cf. Figure 4) and may be explained by differences in metal surface potentials of the tip and sample surface.

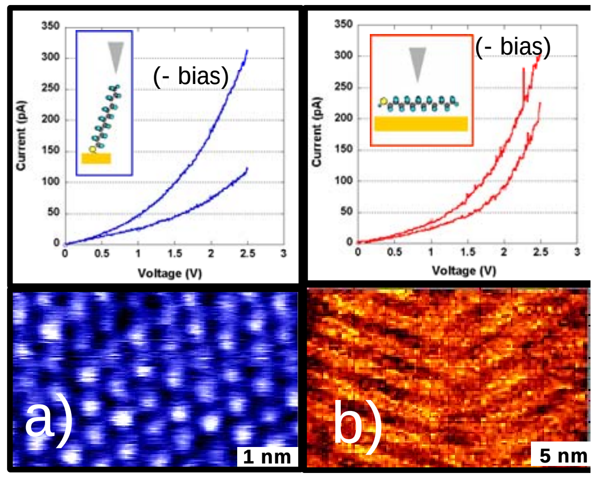


Fig 4. Orientation dependence on tunneling behavior in dodecanethiol showing asymmetric I-V behavior in molecules standing up on the surface (a) vs. more symmetric behavior in molecules laying down (b).

Spectroscopic Measurements. The configuration of molecules within and the electronic structure of electrically-active molecules are believed to be governing factors in molecular conductance. To investigate whether these molecular properties are related to the test-structure measurements, ultrafast laser spectroscopies have been used to study the geometry and electronic structure of moletronic films. The electronic structure of these films was studied using one- and two-photon photoemission.

Specifically,oligo(para-phenylene-ethynylene) thiolate chemisorbed on gold surfaces was studied. Within 5 eV of the Fermi level, four states were observed, two occupied (2.0 eV and 4.0 eV below the Fermi level–B/B*) and two and two unoccupied (3.2 eV and 5.3 eV above the Fermi level). This information is shown schematically in the energy level diagram (Cf. Figure 5) The two states closest to the Fermi level are assigned to a pi-conjugated molecular orbital along the backbone of the molecule, and the other two are assigned to

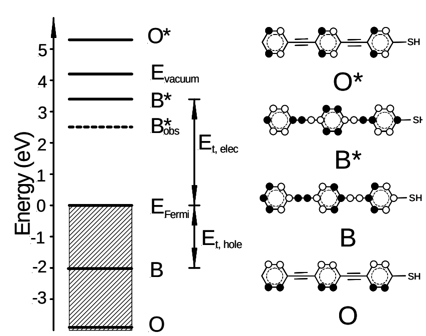


Fig 5. Energy-level diagram for OPE chemisorbed on Au.

molecular orbitals formed by the "ortho" carbons. (See schematic representation of these orbitals in Figure 5.) From this assignment, the hole- and electron-barriers can be determined. These are, respectively, 2.0 eV and 3.4 eV. The charge transport gap can also be estimated. It is between 3.7 eV and 5.4 eV, depending on the criteria used to determine the onset of transport.

Impact: This project is providing detailed insight into the complex behavior of electronic transport through molecules. The program combines for the first time detailed theory and molecular scale measurements that can provide a basis for the complete understanding of electronic structure and transport effects in molecular electronic systems. The foundation that these results provide not only benefits the development of molecular electronics applications, but also affords a groundwork for the investigation of molecular based optoelectronic device applications.

Future Plans: On the horizon are experiments aimed at probing the electrical behavior of ensembles of molecules based on patterning to afford a means of assessing molecular function in device level measurements, as well as scaling conductance properties in molecular ensembles. Future work will be aimed at correlating compression effects on the tunneling properties as investigated by conducting probe atomic force microscopy. The results from these experiments will be compared to theoretical models and to the performance of device-prototypes fabricated and tested by our collaborators in NIST's Semiconductor Electronics Division (812). The photoemission work will systematically investigate the effects of chemical substitute on the molecular orbitals. Theoretical modeling of the transport properties and the valence structure of these electrically-active compounds is also underway.

Low Gas Flow Measurement Assurance Program

Authors: *J. D. Wright and G. L. Kline*

Program: Industrial and Analytical Instruments and Services

Abstract: A Measurement Assurance Program (MAP) was concluded in September, 2003 that compared the gas flow standards of Department of Defense (DoD) laboratories to each other and to the national gas flow standards at NIST. Two sets of four laminar flowmeters (Molblocs manufactured by DH Instruments[1]) were used as the transfer standards (TS) during the MAP. The 8 transfer standards were calibrated between 0.04 and 30 L/min on more than 10 occasions at NIST, over the 2-year period of the MAP, and were calibrated by the participating labs as well. The participating labs were the Air Force Primary Standards Laboratory, the Army Primary Standards Laboratory, the Marine Corps Logistics Laboratory, and DH Instruments in Phoenix, Arizona.

Figure 1. The transfer standard with its laptop data acquisition computer.

Purpose: Compare the DoD and DHI labs with each other and to the NIST standards and evaluate the Molbloc laminar flowmeters for calibration stability, gas specie effects, and suitability as working or reference standards to calibrate other flowmeters.

Major Accomplishment: The uncertainty of mass flow measurements made with the transfer standard (including 2-year reproducibility) were 0.13% to 0.23% on flow range of these data.[2] Differences between individual labs and NIST were as large as 3%, but generally values of 0.6% or less were observed. The flow differences at one of the tested flows (1 L/min) are graphically presented in Fig. 2. In this plot,

[1] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

[2] Unless otherwise stated, uncertainties herein are $k = 2$ or approximately 95% confidence level values.

made with data collected independently from two flowmeters at the same flow, separation between labs (A, B, C, etc.) along the diagonal represents systematic differences. The NIST reference value at (1,1) has error bars proportional to the 2-year reproducibility of the transfer standard. The transfer standard reproducibility in each lab is shown with error bars as well. The differences between labs were generally within the uncertainty expectations (0.16% to 0.55%), but in several cases, changes in the participants' facilities or procedures were recommended that would improve their calibration results. The DoD participants used piston provers, and significant differences in data scatter were discovered depending on the design of their provers.

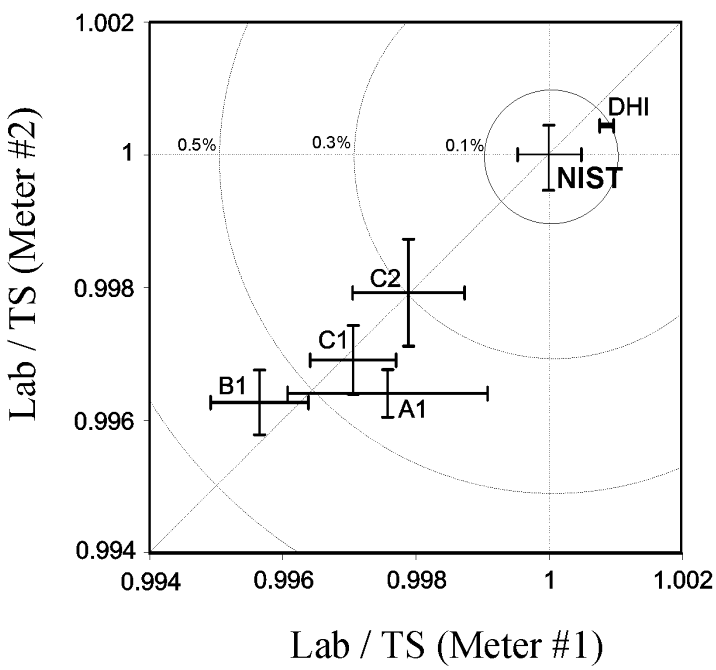


Figure 2. A Youden plot for the 1 L/min comparison data, all labs.

Data quality measures for the transfer standard were very good. Molbocs arranged to flow in series consistently agreed within 0.06% or less and the repeated calibrations at NIST indicated calibration changes of less than 0.1% for all of the Molblocs, even after the rigors of shipment between all the labs. Methodologies for calibrating the Molblocs in one gas, then using them in another gas were demonstrated to agree within ±0.15%.

Impact: The comparison showed where uncertainty improvements could be made, demonstrated flow measurement proficiency, and established flow traceability from the U. S. national standards to the participants. This improves the accuracy of flow measurements made by end users and assures that the participating labs' uncertainty specifications are met under all the actual, dynamic conditions of measurement.

Future Plans: The DoD sponsors will make the transfer standard available for other laboratories to use in their efforts to maintain proficiency and traceability to NIST.

Natural Gas Flow: North American Laboratory Comparison Project

Authors: P. I. Espina and W. F. Guthrie (898)

CSTL Program: Energy

Abstract: This year, 750 billion cubic meters of natural gas will be consumed in the USA (24% of our energy needs). Consumption is projected to increase by 50% by the year 2025. Understanding the importance of accurate natural gas metrology in this country, the natural gas industry requested that NIST develop a round robin testing program to ensure the quality of measurements in the three major natural gas flow calibration facilities in North America: namely, the Colorado Engineering Experiment Station, Inc. (CEESI), Ventura, IA, TransCanada Calibrations Ltd. (TCC), Winnipeg, Canada, and Southwest Research Institute (SwRI) Metering Research Facility, San Antonio, TX.

Purpose: Establish the degree of equivalency between the flow calibrations provided to the North American natural gas industry.

Major Accomplishments: With the support of Daniel Industries (a flow meter manufacturer in Houston, TX), NIST developed the transfer standard package used in this laboratory comparison (see Figure 1). The transfer standard was composed of a turbine meter separated from a multi-path ultrasonic flow meter by a flow conditioner. The transfer standard had a diameter of 300 mm, a length of 9.7 m, and a weight of 4,000 kg (making it one of the largest transfer standards ever used in a NIST program).

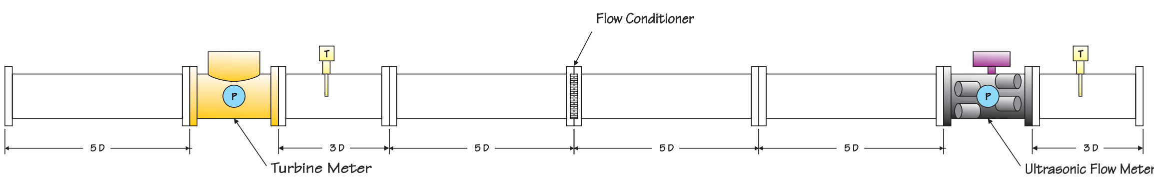


Figure 1. Schematic of transfer standard package (flow from left to right).

Figure 2. **NIST sensor package.**

The transfer standard package, which has volumetric flow range from 726 to 6,169 actual m^3/hr, was instrumented with a NIST-developed sensor package, which included, pressure, temperature, and frequency instrumentation controlled by a laptop computer.

After agreement among the stakeholders, the transfer standard was extensively tested prior to the start of the comparison to assess and quantify its repeatability, with hysteresis effects, itsday-to-day, flow-no flow-flow, and mount-dismount-mount reproducibilities, and its sensitivity to flow profile effects. With this knowledge, the transfer standard was used to compare the performance of the laboratories by testing on 5 occasions: SwRI (Oct. 2002) – CEESI (Nov. 2002) – CEESI (May 2003) – SwRI (May 2003) – TCC (Aug. 2003). In addition, the package was tested for pressure effects at SwRI which was the only laboratory capable of varying line pressure. PMD and SED staff, in preparation for publication in early 2004, are currently evaluating the test results of the comparison.

Impact: The first quantitative assessment of the comparability of flow calibration results of the major natural meter testing and calibration laboratories in the US and Canada will provide improved custody transfer capability to the North American Gas industry. The flow calibration facilities have additional information available to best direct future capital investments to improve the quality of their calibrations. This should lead to reduce uncertainty in the metrology of natural gas in the USA.

Future Plans: NIST is to produce a final report on this project by January 2004. The results will be used to: (i) level of comparability is being quantified to improve future performance of these calibration laboratories, (ii) guide future laboratory comparison projects, and (iii) serve as a guide to the upcoming CIPM Key Comparison on natural gas flow being led by PTB/Germany and NMi/Netherlands.

Nanowires on Microhotplates

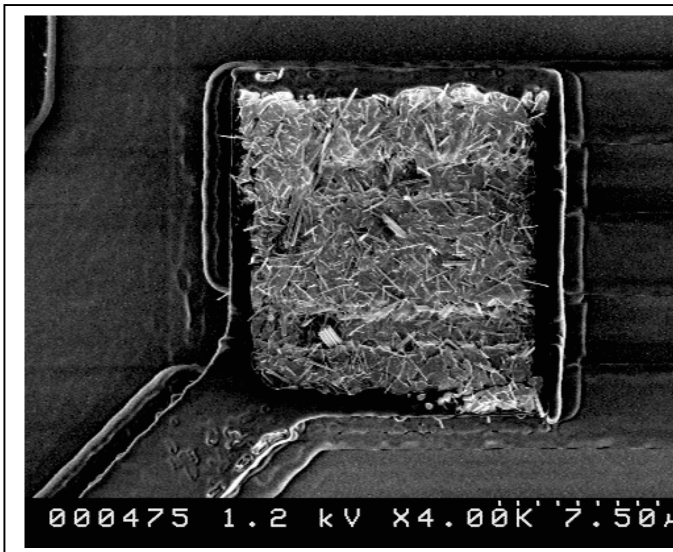
Authors: R. E. Cavicchi, B. Nikoobakht (837), S. Stranick (837), and C. Montgomery

CSTL Program: Industrial and Analytical Instruments and Services

Abstract: Chemical sensing devices based on nanowires and nanorods hold great promise for applications in chemical sensing. Small size implies that a greater fraction of atoms of these nanomaterials lie near the surface, where interaction with the environment can provide measureable changes in the electrical and optical properties. Of particular interest is the concept of a nanolaser, where the dimension of the optical element is small compared to the wavelength of light. Lasing has only been observed in nanorods by optical pumping for a few systems, and only once by the much more practical electrical-driven pumping for a device geometry that is suitable only for demonstrations. A key issue in the development of nanodevices is the establishment of electrical contacts. This work demonstrates the growth of ZnO nanorods on the electrical contact of a microhotplate. The use of the microhotplate anticipates work in which microheater-activated chemical vapor deposition is used to grow heterostructures on the nanorods, as well as for temperature-controlled device operation.

Purpose: To develop a chemical sensing technology based on nanoscale devices for applications in biosensing, environmental monitoring, and homeland security.

Major Accomplishment: There has been much excitement recently over the development of growth methods for nanowires for optical materials. Based on techniques used to prepare carbon nanotubes, these methods involve the use of finely dispersed metal catalysts which promote the growth of crystals in one dimension from a vapor that passes over them. This work represents the first formation of nanowires on the electrical contact of a micromachined structure. Vapor phase transport of ZnO powder in argon was used to deposit ZnO nanowires on a microhotplate prepared with an ultrathin film of gold metal islands. Growth temperature was 1000 °C. Nanowires of average diameter 50 nm were observed on the tungsten-based contact pads of the microhotplate. The growth was selective to the contact pads.



Impact: This work demonstrates that ZnO nanowire structures can be grown selectively on the contact pads of a microhotplate or similar thermally-agile MEMS structure. This shows the compatibility of nanowire growth with MEMS (microelectromechanical systems) devices and establishes a mode for producing electrical contacts.

Future Plans: We plan to investigate the growth of GaN-based nanowires using similar methods. The gallium based materials are especially promising for nanolasers because of the demonstrated feasibility of both n and p-type dopings, required for electrically driven nanolasers. A paper is planned by the beginning of calendar year 04

Temperature Gradient Focusing for Biological Assays in Microchannel Systems

Authors: K.M. Balss, D.J. Ross, M.J. Tarlov; H. Begley (863), K.G. Olsen (Loyola College)

CSTL Program: Health and Medical Products and Services

Abstract: Temperature gradient focusing (TGF) has been used to perform a fast, simple nucleic acid assay that is easily incorporated in capillary or lab-on-a-chip formats. TGF offers three significant advantages for capillary or microfluidic assays. First, targets present at trace levels can be concentrated before the assay reaction to enhance sensitivity. Second, because TGF focuses targets to a fixed point, they can be held stationary for mixing with a recognition probe transported by bulk flow. The facile mixing of reactants shortens analysis time. Third, probe-target binding partners formed in the assay are focused and concentrated at a point spatially distinct from that of the focused targets resulting in sensitive, low-background detection.

Purpose: The project was performed to take advantage of two powerful features of TGF, the ability to concentrate charged analytes and to hold analytes stationary in a microfluidic channel for mixing and subsequent binding with a probe molecule by bulk flow of the probe through the analyte zone. In addition, by using a relatively simple nucleic acid assay for establishing proof-of-concept, the general TGF assay strategy is validated for many other biological assays.

Major Accomplishments: The major accomplishment on this project for fiscal year 2003 was demonstrating the use of TGF for biological assays. To demonstrate proof-of-concept, an assay for DNA was developed using peptide nucleic acids (PNA). PNA molecules contain the same nucleobases as DNA and, thus, exhibit similar base-pairing properties as DNA; however, unlike negatively charged DNA molecules, PNA is neutral. In the TGF assay, the PNA molecules serve as molecular recognition probes for a specific single-strand DNA (ssDNA) sequence. The assay involves three steps. First, the negatively charged ssDNA targets, the analyte molecules, are focused and concentrated at a predetermined point in the capillary. Second, fluorescently labeled PNA is then introduced in the capillary and carried by bulk flow of the buffer through the focused ssDNA. Third, if PNA/DNA hybridization occurs (i.e., the ssDNA is complementary to the PNA) the negatively charged ssDNA/PNA duplex focuses to a different location from that of the ssDNA because of its different eletrophoretic mobility and a fluorescent band is observed. If the ssDNA is not complementary to the PNA, a focused fluorescent band is not observed because the neutral PNA is not focused by TGF.

Impact: A manuscript describing the new method has been submitted for publication to the Journal of the American Chemical Society.

Future Plans: The TGF approach described here using PNA to recognize nucleic acids could be extended to other biological assays such as measurement of protein/protein, nucleic acid/protein, or drug/target binding. The only requirement to implement the TGF assay is that binding of a recognition probe to the target results in an electrophoretic mobility of the complex that is significantly different than that of either the probe or target.

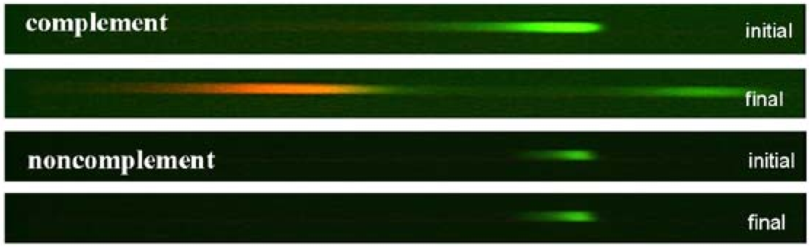


Fig. 1. Fluorescence micrographs of focused DNA and PNA/DNA in a microcapillary. In the experiment the ssDNA is first focused by TGF. PNA is then introduced into the channel by bulk flow while the concentrated zone of concentrated ssDNA is held stationary by TGF. The ssDNA is labeled with a green fluorescent dye, while the PNA is labeled with an orange fluorescent dye. The top two fluorescence images are those obtained after focusing of the perfect ssDNA complement (initial) and then 15 min after introduction of the PNA (final). The bottom two images are control experiements where ssDNA target that is noncomplementary to the PNA is first focused (initial) and then the PNA is flowed for 27 minutes (final). Because the neutral PNA does not bind to the ssDNA, a focused orange spot is not observed in this case. Each image is ≈ 2 mm long. In these experiments the ssDNA targets were fluorescently labeled to confirm that the PNA/DNA duplexes are focused to a different location. In a real assay, it would not be necessary to label the ssDNA targets.

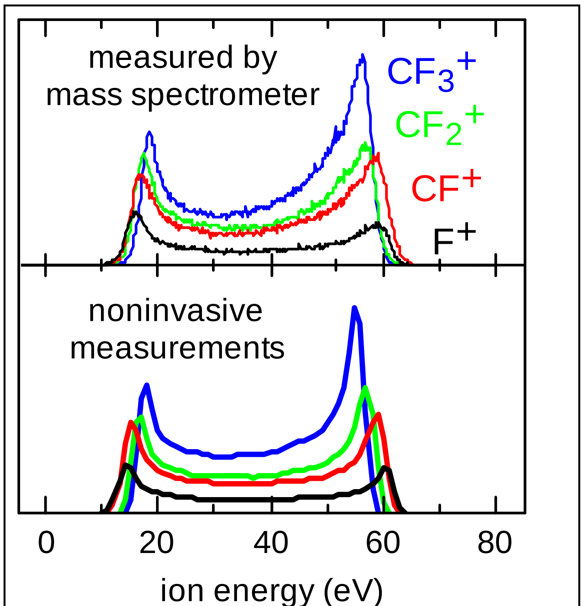
Development of Plasma Process Monitoring and Diagnostic Techniques for the Semiconductor Industry

Authors: M. Sobolewski and K. Steffens

CSTL Program: Microelectronics

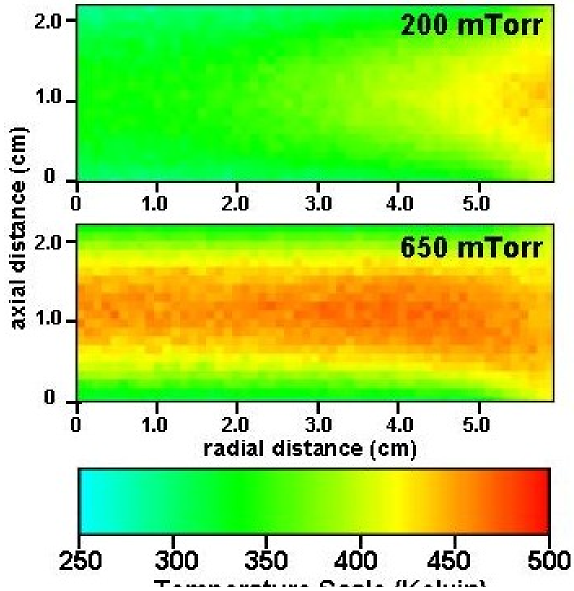
Purpose: The goal of this project is to develop advanced measurement methods, data, and models needed to characterize plasma etching and deposition processes important to the semiconductor industry, enabling continued progress in process optimization, process control, and model-based reactor design. Plasma processing reactors have historically been designed and operated using empirical methods alone, but continued evolution of these tools requires a much greater reliance on process and reactor modeling. Indeed, model-based process design and control is an important need 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.

Major Accomplishments: One major area of activity has been the development and testing of a model-based technique for in-situ, real-time monitoring of ion energy distributions and total ion flux. The technique relies on radio frequency (rf) current and voltage measurements made outside of a plasma reactor, and thus it is well-suited for process monitoring applications in manufacturing where the use of invasive probes to measure ion energy or flux is not practical. Recently, tests of the technique were performed in argon and CF_4 discharges. The tests included a complete sensitivity analysis which quantified the dependence of ion energies and other outputs on all required input parameters, allowing us to rigorously determine the uncertainties in the outputs. Also, recent experiments have demonstrated the application of the technique to real-time monitoring of process drift in an inductively coupled plasma reactor. The drift occurs due to the deposition of a conductive layer on the surface of the dielectric window adjacent to the inductive source. Changes in the conductive layer produce large changes in ion flux and ion energy which are accurately monitored in real-time by the model-based technique.



Ion energy distributions measured by the non-invasive, model-based technique (bottom) and by a mass spectrometer (top).

As model-based reactor design and process development become increasingly utilized, species density measurements and gas temperatures can provide important input and validation for plasma modelers. Spatial variations in plasma temperature can cause spatial differences in gas density and reaction rates and can complicate the interpretation of gas density measurements. The planar laser-induced fluorescence (PLIF) technique not only provides two-dimensional (2-D) density maps of important fluorocarbon radical species in dielectric etching plasmas, it also has been extended to enable 2-D temperature mapping in fluorocarbon plasmas. Using PLIF of the CF radical, temperature maps have been measured in CF_4 plasmas as a function of pressure and power. Temperature has been observed to vary spatially by up to 150 K in these plasmas. Temperature increases with pressure and power and is lowest near the cooled electrode surfaces. In addition, the presence of a silicon wafer was found to increase the temperature throughout the plasma, especially when heat transfer between the wafer and the cooled electrode surface was poor.



Temperature maps of CF_4 plasmas.

Impact: Measurement techniques, data, and models provided by NIST continue to assist our customers in industry to improve their plasma modeling and characterization efforts. Recent examples include NIST-developed electrical analysis techniques that are used by an equipment manufacturer to improve tool-to-tool reproducibility and adapt existing process recipes to next-generation plasma reactors. In addition, the web-based NIST Electron Interactions with Plasma Processing Gases database continues to distribute fundamental data to plasma modelers in industry and academia world-wide.

Future Plans: Future plans include the further development of model-based process monitoring techniques and optical diagnostics, including experiments to be performed in a plasma reactor operated in the dual-frequency capacitively coupled mode used in state-of-the-art, industrial oxide etchers.

Micellar Affinity Gradient Focusing

Authors: D. Ross, and K.M. Balss; and W.N. Vreeland (839), and P.B. Howell (839)

CSTL Program: Health and Medical Products

Abstract: To meet the outstanding need for effective pre-concentration techniques for microfluidics, a new focusing method, Micellar Affinity Gradient Focusing (MAGF), was invented. The new method is the first electrokinetic focusing method that provides the ability to concentrate and separate analytes based upon properties other than electrophoretic mobility or isoelectric point. Initial experiments indicate that MAGF can provide a simple method for focusing classes of analytes – such as neutral analytes – that cannot be electrophoretically focused by other means.

Purpose: This project was initiated to address one of the outstanding problems in the field of microfluidics: the need for effective methods of pre-concentration suitable for miniaturization and integration into 'lab-on-a-chip' platforms and that can be applied to a wider range of analytes than is allowed by current techniques.

Major Accomplishments: The major accomplishment on this project for fiscal year 2003 was the invention of MAGF, a new method for the focusing and concentration of hydrophobic and neutral analytes in microfluidic channels or capillaries. MAGF works by creating a gradient in the retention of the analyte into the micelles as illustrated in Fig. 1. On one side of the retention factor gradient, the analyte is strongly partitioned into and moves with the micellar phase. On the other side, the analyte is weakly partitioned into the micellar phase so that it moves with the mobile phase (buffer). Using charged micelles and the combined application of an electric field and a pressure gradient, the micelles can be made to move from the region of high retention to the region of low retention while the mobile phase moves from the region of low retention to the region of high retention. When this is done, the net velocity of the analyte will be positive on one side of the gradient and negative on the other side and zero at some point in the middle. Analyte will then move towards the zero-velocity point from both directions and be focused and concentrated there. Different analytes, with different affinities for the micellar phase, will be focused at different points along the channel, so that the method provides a focusing mode analog to micellar electrokinetic chromatography (MEKC) separation. Unlike previously described focusing separation methods (such as isoelectric focusing (IEF), electric field gradient focusing (EFGF), or temperature gradient focusing (TGF)), MAGF provides for separation of analytes based on properties – such as hydrophobicity – that are not related to the electrophoretic mobility. Consequently, it can be used to focus neutral and zwitterionic molecules that cannot be focused by previously described methods (see Fig. 2).

Impact: The new method was first presented at the Gordon Research Conference on Microfluidics and at the microTass 2003 conference, and was well received. A manuscript describing the new method has been submitted to the Journal of the American Chemical Society.

Future Plans: Because of the promising nature of the initial demonstrations of MAGF, research on this project will continue with emphasis on proving the method further by applying it to current problems in analytical chemistry and biochemistry.

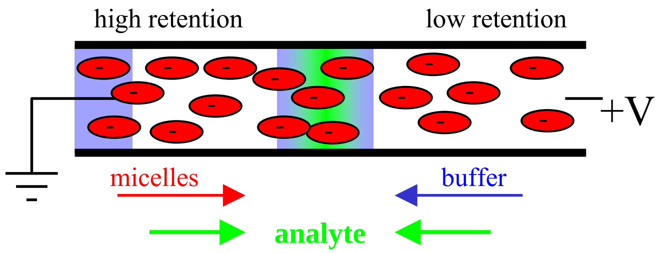


Fig. 1. Schematic of micellar affinity gradient focusing in a microchannel or capillary.

Fig. 2. Micellar gradient focusing and separation of two zwiterionic fluorescent dyes, rhodamine B (red) and rhodamine 110 (green). For scale, the image is 2 mm long.

Outreach Activities in Thermometry

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

Program: Industrial and Analytical Instruments and Services

Abstract: By sponsoring conferences and presenting workshops, the NIST Thermometry Group educates industrial users and fosters communication within the field of thermometry. In FY2003, the Thermometry Group sponsored the premier conference on thermometry, the 8th International Temperature Symposium. The proceedings of these Symposia are valued for their documentation of the state of the art in thermometry. We also provided training to industry, through a workshop for the ASTM committee on Petroleum Products and through workshops at the NIST campus in Gaithersburg.

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: In October, 2002, NIST again sponsored the International Temperature Symposium, which is held once a decade. Held over four days, with over 200 presentations and over 300 participants, this event is the premier scientific conference in thermometry. Staff of the NIST Thermometry Group organized all aspects of the technical program of the Symposium. The hard-bound proceedings, carefully edited by NIST staff, are renowned as an archival source of thermometry research results. Such an event is tailored to those with a high professional interest in thermometry; we also support more casual users. For example, in December, 2002, we presented a workshop on "Using a Liquid-in-Glass Thermometer in Industrial Environments" to the members of ASTM committee D-2 on Petroleum Products and Lubricants. In two separate sessions in Anaheim, California, over 120 D-2 members attended the workshop. Additional workshops are regularly offered at the NIST campus in Gaithersburg. Presented once or twice a year over the past two decades, the Precision Thermometry Workshop provides training in all facets of contact thermometry. A recent supplement to this course is the Fixed-Point Cell Mini-Workshop, held approximately once each year.

Impact: Because of our outreach activities, the NIST Thermometry Group is world-renowned as a source of thermometry expertise. U.S. industry has attained a level of sophistication in thermometry that is commensurate with many foreign National Metrology Institutes, partly because of ready accessibility to methods established at NIST.

Future Plans: Additional mini-workshops, featuring small class sizes and extensive laboratory exercises will be developed for liquid-in-glass thermometers and for calibrations by comparison methods. For the first time, the Thermometry Group will be delivering a workshop at the Measurement Science Conference in 2004.

Johnson Noise Thermometry Competence Project

Authors: W. L. Tew, S. W. Nam (Div. 814), S. Benz (Div. 814)

Program: Technologies for Future Measurements and Standards

Abstract: The NIST prototype system for Johnson Noise Thermometry (JNT) has undergone recent improvements which have resulted in higher measurement accuracy in both the relative and absolute modes of operation. The improvements are primarily in the Quantized Voltage Noise Source (QVNS), a calculable noise power reference produced by digital synthesis using a pulse-driven Josephson array. The latest data using the prototype system have demonstrated a 0.01 % standard uncertainty in relative noise power and 0.025 % uncertainty in absolute (SI) noise power. These results have been achieved in an unshielded environment at NIST's Boulder Labs as verified through use of a gallium triple point cell and water triple point cell to establish known temperatures. A second digital power correlator has also been constructed which will allow the original system to be sent to Gaithersburg for use in special shielded facilities there. The ultimate applications are in both high-temperature contact metrology and in certain demanding industrial environments where either remote, long-term test, and or harsh conditions limit the use of conventional artifact thermometers.

Purpose: JNT is a primary technique which is well suited to certain demanding application environments and as a high-temperature contact method for thermodynamic determinations relative to the International Temperature Scale of 1990 (ITS-90). JNT is the only established thermodynamic method in contact thermometry which remains practical for applications above 800 K. Johnson noise temperature probes can be designed to sample the thermal noise from noble-metal alloy resistance elements up to at least 1800 K; such elements are relatively insensitive to changes caused by thermal strains or diffusion of impurities. The NIST JNT technique represents an important innovation by applying Josephson-based voltage standards to create an intrinsically calculable noise source, the QVNS. This approach conveys key operational advantages over conventional JNT methods already in use at other NMIs, and allows a fixed-point-independent method of measuring SI temperatures.

The new NIST technical approach is being developed to help move JNT into wider use in both the industrial and metrology domains. For NIST temperature metrology, the new JNT system is competitive with radiation-based methods for T<1235 K. For industrial applications, the NIST method could be tailored to the use of solid-state noise references for those application environments where thermometric stability is critical and serviceability is limited, such as power generation plants and chemical processing applications. This will benefit all users of temperature instrumentation who are engaged in accuracy-critical applications limited by artifact thermometer performance.

Major Accomplishments: New circuit designs of the Josephson QVNS have dramatically reduced the common mode voltage error measured by the Johnson noise measurement electronics. This has enabled a significant improvement in the demonstrated accuracy of new NIST methodologies. The new accuracy benchmarks are relative to ITS-90 assignments for the verification test fixed points: 1) the gallium triple point (GaTP, 302.916 K) ; and 2) the water triple point (WTP, 273.16 K). These fixed points establish ITS-90 temperatures which are compared to the JNT-derived temperatures. The latest data demonstrate an uncertainty of 250 μK/K in the absolute mode and 100 μK/K in the relative mode for the T(GaTP)/T(WTP) ratio. These results are within the current combined estimated uncertainties for those measurements. For the relative mode data, the agreement with the ITS-90 value is within the JNT statistical precision alone as estimated by the available data.

Construction has begun on a low-noise comparison furnace for use between 273 K and 934 K which will enable comparisons of JNT-based temperatures with ITS-90 over that range. The comparison furnace will be installed in the Division 836 electrically shielded room facility. A second set of digital correlator electronics has been built to allow two systems to be operated, one in Boulder and the other in Gaithersburg.

Impact: The achievement of an uncertainty of 0.001 % in the relative mode will be competitive for temperature metrology applications above ~700 K. New thermodynamic data in the overlapping ranges of contact and radiation-based thermometry between 700 K and 1235 K would be a significant input for the next international temperature scale. In certain industrial areas, JNT systems based on solid-state noise references could eventually reduce the cost-of-operation of any process that is limited by the calibration stability of artifact-based thermometers. Here 0.1 % to 0.01 % uncertainties are sufficient, depending on the specific application.

Future Plans: CSTL plans to use the JNT prototype system, with a QVNS provided by NIST's Electronics and Electrical Engineering Laboratory (EEEL), to determine the differences between JNT-determined temperatures and temperatures on the ITS-90 over the range of the comparison furnace (273 K and 933 K). EEEL plans involve the continued refinement of the QVNS and development of a custom programmable arbitrary bit stream generator, a key component to improving noise and other waveform synthesis capabilities.

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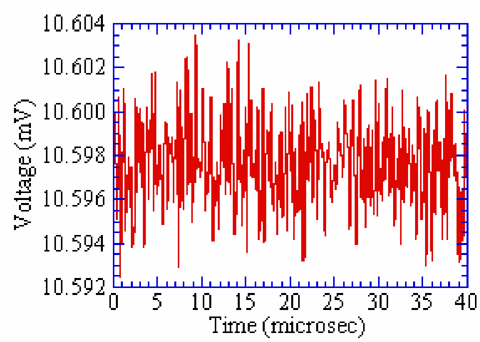


Fig. 1. A pseudo-noise trace as produced by the QVNS with a 1.6 kHz repetition rate

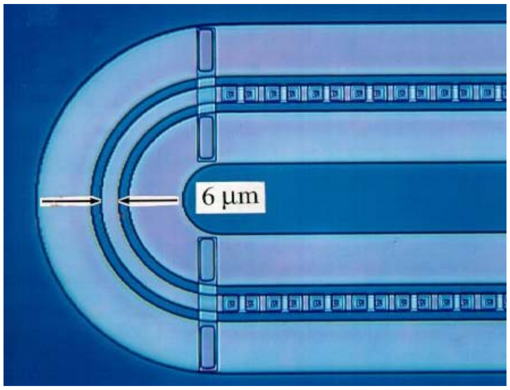


Fig. 2. Magnified image of a section of a Nb-PdAu-Nb Josephson array.

Proficiency Testing and Measurement Assurance for the International Temperature Scale of 1990 (ITS-90)

Authors: G.F. Strouse, D.C. Ripple

Program: Industrial and Analytical Instruments and Services

Abstract: An increasing number of companies are seeking accreditation through NIST's National Voluntary Laboratory Accreditation Program (NVLAP) for ITS-90 Standard Platinum Resistance Thermometer (SPRT) calibration services with uncertainty claims that are smaller than those of many National Metrology Institutes (NMIs). In order for NVLAP to grant accreditation to those companies and for those companies to gain acceptance in the global marketplace, validation of the submitted uncertainty claims is critical. For that purpose, the NIST Thermometry Group developed a tiered proficiency testing program and service that is designed with several levels of proficiency testing that are commensurate with the submitted uncertainty claims. At the lowest uncertainties, the level of scrutiny is comparable to that which an NMI undergoes for international acceptance. The newly developed symbiotic relationship between the NIST Thermometry Group and NVLAP in the arena of proficiency testing for ITS-90 SPRT calibrations services will improve the international acceptance of NVLAP accreditations and uncertainty claims by industry.

Purpose: The use of proficiency testing is an integral aspect of the accreditation process to validate the claimed uncertainties of companies seeking accreditation. A number of companies claim calibration uncertainties for ITS-90 SPRT calibrations that are in many cases lower than that of foreign NMIs. In such cases, for uncertainty claims to be accepted in the global marketplace, the level of proficiency testing must match the level of scrutiny that an NMI undergoes for international acceptance of its national standards. The tiered NVLAP proficiency test program provided by the NIST Thermometry Group allows a U.S. company to undergo a proficiency test at a level that is commensurate with their uncertainty claims without being an undue burden.

Major Accomplishments: A new proficiency testing program was developed by the NIST Thermometry Group for companies seeking NVLAP accreditation for ITS-90 SPRT calibrations. A selection matrix, with specific cutoff values based on an analysis of the uncertainties of numerous NMIs, is used in conjunction with the submitted uncertainty claims to determine the appropriate proficiency test. The proficiency tests range from calibration of a single SPRT (large uncertainty claims) to a combination of a measurement assurance program (three SPRTs) and the direct comparison of fixed-point cells (NMI level uncertainty claims). Protocols and report forms were designed to maximize confidence in the results and transparency of the interpretation. The new program was created and implemented in the past year within the NIST Thermometry Group to meet the growing needs of NVLAP. A prototype NVLAP proficiency test was performed with a U.S. company to test the new service, with results seen in Figure 1.

Impact: Cultural and technical differences have led to conflicts in the international acceptance of accreditation and calibration uncertainties. Proficiency testing provides the concrete evidence necessary for objective evaluation of a laboratory's capabilities. The design and implementation of the NIST proficiency testing program in thermometry assists industry in achieving accreditation and international acceptance, and furthers confidence in the quality of industrial measurements. The NIST Thermometry Group continues to be the only laboratory capable of meeting the proficiency test and measurement assurance demands of the U.S. temperature community.

Future Plans: The number of available test artifacts will be increased in FY 2004 by 30 % to accommodate the increased demand for this new service area. During FY 2004, proficiency testing of thermocouples and industrial thermometers will be implemented.

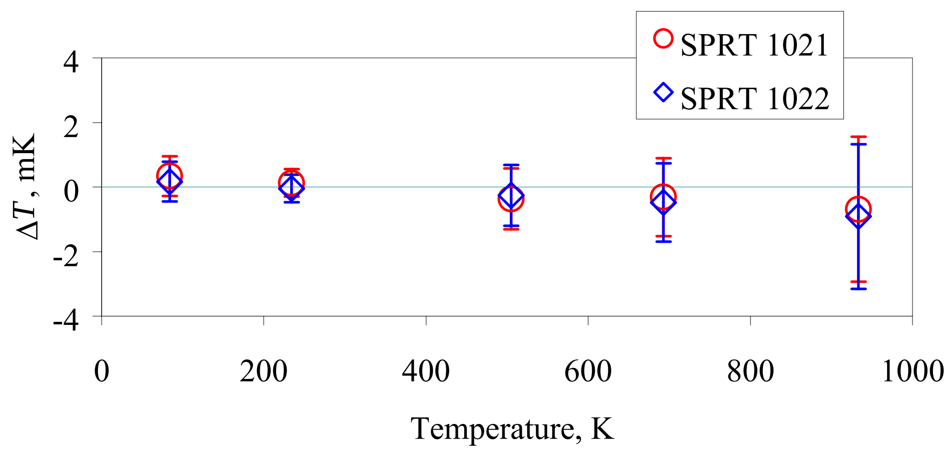


Figure 1. Sample results of a proficiency test. ΔT is equal to the participant calibration results minus the NIST results; error bars indicate the combined expanded uncertainty (k=2) of the comparison.

Proximity Effects of Lightpipe Thermometers in Rapid Thermal Processing Tools

Authors: K. G. Kreider, W. A. Kimes, D. P. DeWitt (844), B. K. Tsai (844)

Program: Microelectronics

Abstract: Lightpipe radiation thermometers (LPRTs) are used as temperature-monitoring sensors in rapid thermal processing (RTP) tools for semiconductor fabrication. To minimize disturbances in the reflectivity of the RTP chamber, small, 2 mm diameter, sapphire lightpipes are often the temperature sensor of choice. This study was undertaken to measure and model the effect of LPRT proximity on the wafer temperature. Our experiments were performed in the NIST RTP test bed. We measured the spectral radiance temperature with the center lightpipe and compared these measurements with the three LPRTs at the mid-radius of the wafer and the thin-film thermocouple (TFTC) junctions of a NIST calibration wafer. Depressions in the wafer temperature up to 25 °C with the lightpipe at 2 mm spacing were observed. A finite-element radiation model of the wafer-chamber-lightpipe was developed to predict the temperature depression as a function of the lightpipe proximity distance and the chamber-wafer separation. The experimental results were compared with those from a model that accounts for lightpipe geometry and radiative properties, wafer emissivity and chamber cold plate reflectivity.

Purpose: 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. Wafer temperature measurements are frequently performed in a highly reflecting chamber to obtain a near-unity effective emissivity of the wafer. However, the sapphire lightpipe tip has a low reflectivity (high absorptivity) that enhances radiation heat transfer from the target region. This low reflectivity causes a depression in the wafer temperature, degrading the thermal uniformity necessary for fabrication of high-quality semiconductor devices. This project was initiated to quantify the effect of lightpipe proximity to the wafer temperature measurement and to provide a model for use with commercial tools.

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 their temperature sensitivity; developed technology for their *in situ* calibration in the RTP tools using the NIST patented thin-film thermocouple wafer; and measured the effects of wafer emissivity on their measurement results in the RTP tool.

This project defined the effect of lightpipe proximity to the wafer on the temperature distribution of the wafer in our NIST RTP test bed and provided a model to estimate the effect in commercial tools. We measured the radiance temperature of the four LPRTs on two 200 mm wafers at 640 °C to 860 °C in the NIST RTP test bed for a total of 68 thermal cycles. The effect of the lightpipe proximity on the radiance temperature measurement of the center lightpipe was plotted for each wafer at four reflecting shield distances, as a function of temperature. All such curves indicated a near linear increase in center-lightpipe radiance temperature depression as a function of temperature. Typical results are plotted in Figure 1 for the change in the central radiance temperature due to the proximity (3 mm to 6 mm) of the central lightpipe to the wafer for a reflecting plate distance of 10 mm. The lines represent values from the model for proximities of 3 mm and 6 mm.

Impact: The results of this study, which revealed a major systematic effect on the temperature measurement and thermal uniformity of process wafers, 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 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: With the advice of our Common Interest Group, our future research will address two new industrial needs. First, for Post-Exposure Bake processes of photographic resists (100 °C to 160 °C), we will improve the temporal resolution of temperature measurements. Second, we will improve methods for the *in situ* calibration of the new direct-reading LPRTs used for RTP fabrication of silicides (300 °C to 650 °C).

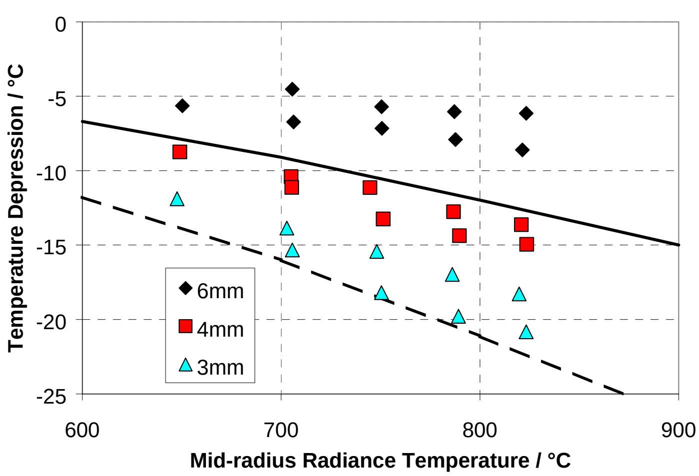


Figure 1. Temperature depression caused by an LPRT at the indicated distances from a wafer. Symbols are measured values. The solid and dashed lines represent values from the model for proximities of 6 mm and 3 mm, respectively.

The NIST Gravimetric Hygrometer: A Primary Humidity Standard

Authors: C. W. Meyer, J. Valencia (Guest Researcher, CICATA, Mexico), G. Scace, J. Hodges

Program: Measurement Standards

Abstract: The NIST gravimetric hygrometer (GH) is a primary humidity standard that determines the concentration of water vapor in a gas sample by independent measurements of the water mass and the mass of the dried gas sample. The GH is now operational; its uncertainties are currently being evaluated and optimized. Performance optimization and uncertainty evaluation are accomplished through both control tests and measurement of the humidity from a well characterized generator.

Purpose: NIST performs humidity calibrations for customers as part of its mission to develop, maintain and disseminate measurement standards. These calibrations are performed by generating samples of gas with well-characterized humidities, which are then supplied to customer hygrometers. To insure the highest quality calibrations, the performance of these generators should be periodically tested by measurement of the generated humidity using a primary humidity standard. The GH was built to fulfill this function.

Major Accomplishments: The NIST GH determines the amount of water in a gas sample by measuring the mass fraction of water in the sample. This is accomplished by trapping the water in collection tubes containing desiccant; the collection tubes are weighed before and after trapping, and the mass difference is due to the trapped water. The mass of the dried gas sample is determined by volume measurements using interferometric measurements of piston displacement (see Figure 1), in combination with gas density calculations. The GH is now operational and its uncertainties are currently being evaluated and minimized. Comparisons with the NIST Low Frost Point Generator and 2-Pressure Generator have determined its present agreement with these generators to be within 0.4 % of water mass fraction. The comparisons have also shown the present day-to-day reproducibility of GH measurements to be within 0.3 %. Control tests have identified methods for further reduction of the measurement uncertainties. Specifically, tests have been performed to determine the water collection capacity of the collection tubes and to accurately account for changes of gas mass in the collection tubes. Additional tests have been designed to determine the amount of residual water in the gas after it passes through the collection tubes.

Impact: NIST now has a primary working standard for humidity that can validate (and perhaps help improve) the performance of the generators used for calibrating customer hygrometers. This helps assure NIST customers that its humidity standards and calibrations are maintained at the levels needed by industry.

Future Plans: Further control tests and modifications of measurement techniques are planned until the uncertainties of the GH measurements are assured at the required levels. Once this process is complete, the uncertainty of the GH humidity determination is expected to be less than 0.1 %. Afterwards, comparisons with the humidity generators will be performed every six months to confirm the performance of the generators. The GH will also be used for measurement of the enhancement factor for water in nitrogen.

Figure 1. Prover tubes with pistons used for the determination of the sample volume.

High-Resolution Cavity Ring-Down Spectroscopy Measurements of Water Vapor

Authors: J.T. Hodges and J.G. Cormier

Abstract: This work, aimed at establishing and disseminating primary measurement standards for trace water, has diverse applications in semiconductor processing, trace gas monitoring and analysis, and atmospheric research. The research supports a broad class of spectroscopic techniques that are based upon the absorption of electromagnetic radiation by water vapor. These techniques require knowledge of H_2O transition line strength, which is temperature dependent, and transition line shape, which depends on total gas pressure and mixture composition. We continue to develop and exploit cavity ring-down spectroscopy (CRDS) to measure spectroscopic properties of H_2O with extraordinary precision. Recently, we have measured transition line shapes and strengths near a wavelength of 940 nm and the temperature dependence of the water continuum absorption at a wavelength of 10 µm. As such, this research provides improved measurement confidence and quantifiable uncertainty for absorption spectroscopy measurements, with results relevant also to the spectroscopic detection of gases other than H_2O.

Purpose: Trace amounts of water vapor occurring in bulk source gases or de-adsorbed from system surfaces can adversely effect important processes related to the growth and manufacturing of semiconductors, photonic devices and other micro- and nano-scale solid state systems. Monitoring of residual water vapor concentration at or near the point of use is thus often needed. To this end, we seek to establish and disseminate primary measurement standards enabling quantitative on-line measurements of water vapor at trace concentrations (~ 10^{10} to 10^{13} molecules cm^{-3}), a domain where gravimetric techniques are inapplicable. This work, which benefits H_2O measuring instrument manufacturers, high-purity gas suppliers and other end-users, supports a broad class of spectroscopic techniques based upon the absorption of electromagnetic radiation by water vapor. Another motivation relates to the role of water vapor as the dominant greenhouse gas in the earth's atmosphere. Thus, a detailed understanding of the water vapor absorption spectrum is necessary for modeling atmospheric and solar radiative transfer, and for developing spectroscopic probes suitable for quantitative measurements of atmospheric H_2O.

Major Accomplishments: In FY 2003, two sets of CRDS experiments covering different spectral ranges were implemented. In the first system, a cw diode laser and a custom high-resolution CRDS apparatus were used to measure absolute line strengths, and line shapes for water vapor transitions in the near-ir. A long-term reproducibility of better than 0.3 % and relative uncertainty less than 2 % in the determination of line strength was demonstrated. See Fig. 1 for a typical spectrum. The effects of pressure broadening and collisional narrowing of the line shape were quantified and a spectral resolution on the order of 1 MHz was achieved, illustrating the high spectral resolution of the CRDS method. The second CRDS experiment considered the water vapor absorption continuum in the mid-ir spectral range. The temperature dependence of the continuum absorption coefficient was measured from –15 °C to 20 °C. This work exploited the high precision of the mid-ir CRDS technique and access to NIST standards of humidity generation and measurement. A detection limit of 30 pmol mol^{-1} was demonstrated. Finally, to complement the mid-ir CRDS studies of the water vapor continuum, similar CRDS measurements of the water vapor continuum were also begun using the near-ir CRDS system. These studies suggest that near-ir CRDS measurements of the water vapor continuum may answer some important scientific questions regarding the role of water dimers in the radiation absorption by atmospheric water vapor.

Impact: This research provides improved measurement confidence and quantifiable uncertainty for absorption spectroscopy measurements in general, with many of the results being relevant to the quantitative detection of arbitrary gases in addition to H_2O. The work is also specifically pertinent to spectroscopic measurements of H_2O in various gaseous media and has diverse applications in semiconductor processing, gas monitoring and atmospheric research.

Future Plans: The near-ir CRDS setup will be modified to; a) realize line shape measurements with better precision via optimization of ring-down cavity operating parameters, b) probe a stronger absorption band of water vapor (for lowered detection limits and expanded spectral coverage), and c) to probe trace quantities of CH_4 (demonstrating applicability of the CRDS method for other important gases).

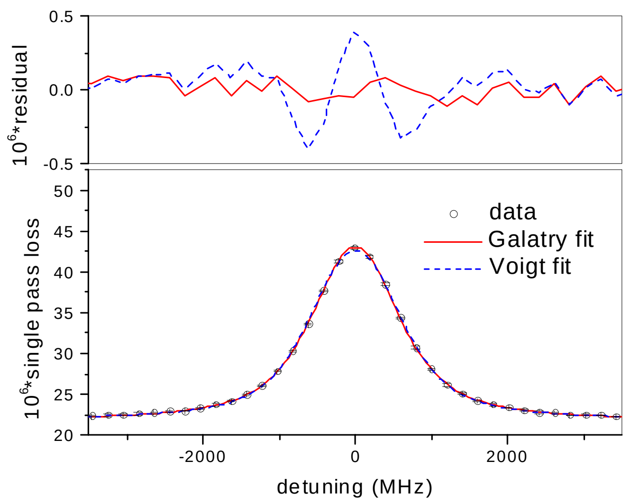


Figure 1. Measured spectrum of H_2O absorption transition. CRDS measurements and best-fit theoretical line shapes (bottom panel), and fit residuals (top panel).

Improved Vacuum Transfer Standards – Ionization Gauges

Authors: P.J. Abbott, P. Mohan (NPL India)

CSTL Program: Industrial and Analytical Instruments and Services

Abstract: Our goal is to disseminate NIST's realization of the Pascal at high vacuum levels directly to our customers and into readily available commercial gauges. However, commercial vacuum transfer gauges are unstable and hamper efforts to effectively disseminate NIST's uncertainties to our customers. In recent years, a new and improved hot cathode ionization gauge has become commercially available. The sole manufacturer claims improved stability over that of a conventional Bayard-Alpert (BA) ionization gauge by up to a factor of 10, thereby making it a superior candidate as a high-vacuum transfer standard below 10^{-4} Pa. Sales have been extraordinary, and the gauge has supplanted conventional BA gauges in many applications and is now widely used throughout the world. However, in the course of two recent rounds of calibrations at NIST, several of these gauges have shown far worse stability (calibration shifts as large as 10 % at the lowest measurable pressures) under certain operating conditions than is reasonable to expect from the manufacturer's literature. Furthermore, the response of the gauge seems to depend strongly on its history of gas exposure. Our work confirms the history dependence of the gauge response and identifies ionic pumping of gas into the gauge walls as the source of the instability. It also suggests a simple method of stabilizing the gauge's response.

Purpose: Until recently, the BA gauge has been the best transfer standard available below 10^{-4} Pa. However, a variant with fortified electrodes and optimized ion optics was introduced in 1993 with an uncertainty of ± 3 % claimed manufacturer, representing a substantial improvement over previous BA gauge designs. However, large shifts in calibration factor have been observed during routine operation, both at NIST and elsewhere, exacerbating the measurement uncertainty. Explanation and elimination of these shifts is critical for customers who use the gauge for process control, as resources may be wasted on inferior product quality or processing delays. Additionally, gauge instabilities may affect international commerce if they lead to inaccurate results when comparing national primary standards.

Major Accomplishments: We have established that ionic pumping of gas by components internal to the gauges is responsible for the shifts in calibration that have been observed. The pumping speed of the gauge was found to be greatest just after a high temperature bake, a common procedure used to achieve high vacuum. It was also found that the gauge could not pump gas indefinitely, but rather became saturated after exposure to a pressure of 10^{-2} Pa for three hours. The gauge response prior to exposure and after exposure differed by up to 10 % at 10^{-6} Pa of nitrogen, over three times higher than manufacturer expectations. Furthermore, the gauge response became stable after exposure, but would revert toward its pre-exposure response if the gauge was pumped on for a long period of time or baked again. Both of these procedures have the effect of purging the gauge of previously pumped gas molecules. It is noteworthy that good short-term repeatability can be achieved via intentional gas saturation of the gauge which "turns-off" the gauge pumping mechanism. Such "conditioning" of the gauges after a high temperature bake and prior to measurements ensures gauge stability. It should also be noted that the ionic pumping effect was observed in two conventional BA gauges, but to a lesser degree than in the new gauges.

Impact: Understanding the effect of ionic pumping on the stability of these gauges will lead to reduced uncertainty in high vacuum metrology, important to industrial process control, secondary laboratory calibrations, and international comparisons of high vacuum standards. Additionally, these results provide important information to the manufacturer for mechanical re-design and/or optimizing operating voltages of the gauge to minimize ionic pumping.

Future Plans: We will explore the gas species dependence of the ionic pumping effect, the pumping capacity of a given gauge, and the effect of altered ion energies on the quantity of gas pumped by the gauge. This information will lead to an improved gauge and provide better quantification of the uncertainty associated with high vacuum measurements.

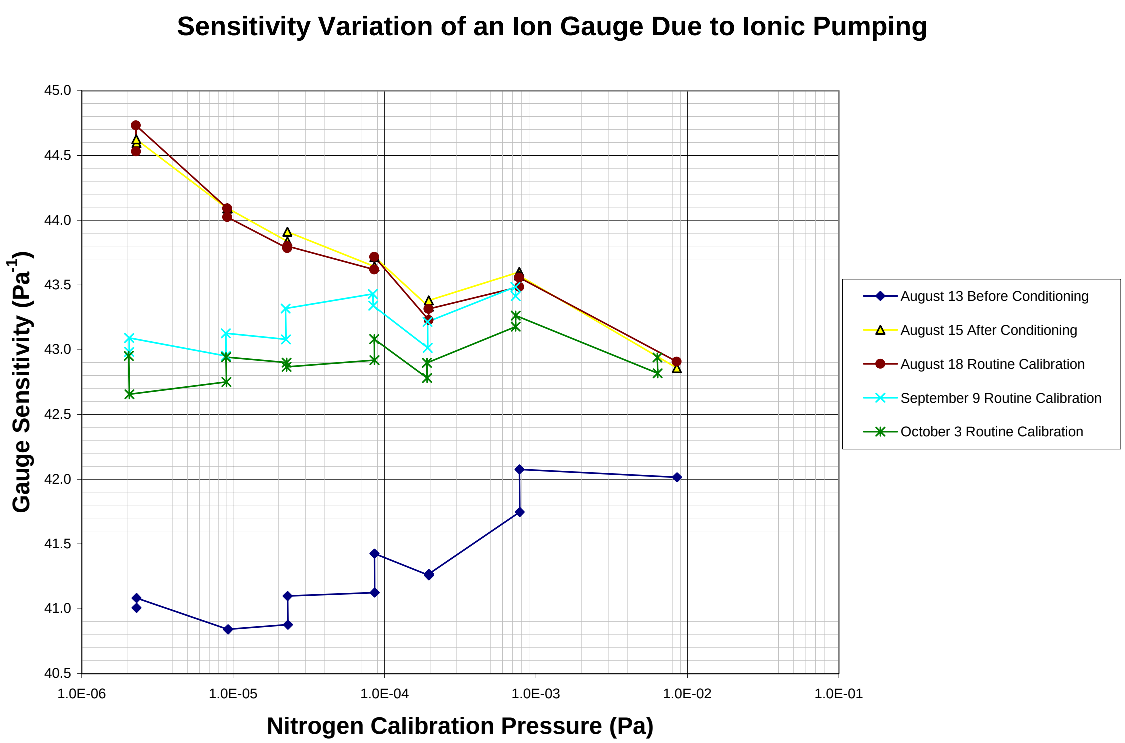


Figure 1. The change in gauge response as a result of ionic pumping. The gauge was conditioned at 10^{-2} Pa for three hours on August 14, 2003. The before and after conditioning data differ by as much as 10 % at the lowest calibration pressures. After August 18, the gauge remained in normal operating mode and was pumped on by the vacuum chamber pump. The data of September 9 and October 3 show a gradual relaxation of the gauge sensitivity to its pre-conditioning response.

Improved Vacuum Transfer Standards – Spinning Rotor Gauge Stability Studies

Authors: R. F. Chang

CSTL Program: Technology for Future Measurements and Standards

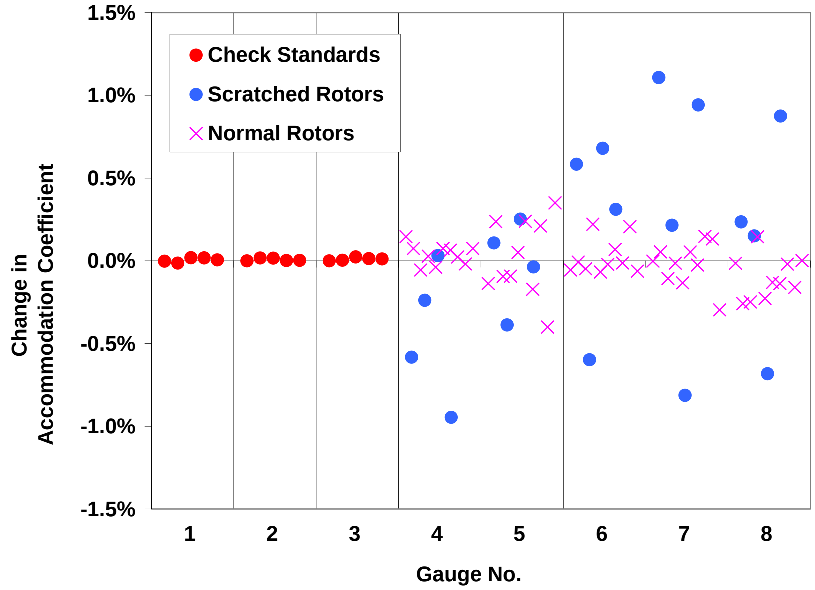
Abstract: Our goal is to disseminate NIST's realization of the Pascal at high vacuum levels directly to our customers and into readily available commercial gauges. However, commercial vacuum transfer gauges are not sufficiently stable to effectively disseminate NIST's measurement uncertainties to our customers. In FY03, we quantified major causes of calibration instabilities in spinning rotor gauges (SRGs), tied to handling procedures of the rotor. A physical model is proposed to explain the calibration instability although explanations for large instabilities observed among customer gauges are not yet completed.

Purpose: The spinning rotor gauge has become the transfer standard of choice for vacuum calibrations from 10^{-4} to 1 Pa due to good calibration stability (changes < 0.5%/year). While internal NIST SRGs exhibit better long-term stability, some calibration customer gauges have shown inexplicably larger shifts. Understanding the sources of these instabilities is important to gauge users, as well as to primary standard laboratories that rely upon high stability for maintaining their Quality Systems and for satisfactory performance as transfer standards.

Major Accomplishments: In FY02, it was observed that de-mounting and re-mounting of the SRG suspension head may cause an average shift of ~ 0.1% in accommodation coefficient (which is directly tied to calibration stability), σ, and in some case as large as 0.4%. However, this did not fully explain observations the 1% and larger shifts in customer calibrations. In FY03, we investigated the effects of various handling procedures which affect surface properties of the rotor, such as their rinsing in cleaning solution, weighing and measuring, mounting and inspecting under a microscope, and even rolling and shaking of the rotor in a thimble to simulating transit between laboratories. Surprisingly, these procedures shifted σ only ~0.25% on average, although customer shifts as large as 0.8% were observed. These and other factors suggest that the large observed shifts in σ are partly a manifestation of a rotational-axis-dependence of σ. Inspection of customer rotors revealed many with non-uniform blemishes (*e.g.*, scratches, corrosion), and some with polar orientations. A series of experiments using deliberately longitudinally-scratched rotors showed an average shift in σ of 0.5%. Shift values ranged from -1% to 1%, as shown in in the figure, when the suspension head was de-mounted and re-mounted. Each new suspension has a different rotational axis for the rotor. The extent of the resulting variability is close to that observed from calibration customers. Three check standards, undisturbed between calibrations, were calibrated along with the scratched rotors. The check standards reproduced σ each time as expected. The data of normal rotors, which have some blemishes but without deep longitudinal scratches, are also shown for comparison.

Impact: We have completed a first-ever, comprehensive investigation into the causes of calibration instability of SRGs, and the findings have refuted many long-held beliefs. Our results can significantly affect the manufacturing processes as well as routine operations and maintenance of SRGs. There are implications for new material selections as well as input into the next generation of SRGs, underway at both NIST and the Forschungszentrum-Jülich in Germany.

Future Plans: Our results suggest a few areas of exploration for improved stability of SRGs. For instance, we need to explore the manufacturing processes of the rotor such that a preferred rotational axis may be established, and the surface is mechanically and chemically hardened to resist corrosion and scratches. Choice of soft materials for the thimble or treatment of its inner surface may also aid in reducing the probability of scratches on the rotor due to sudden loss of suspension.



Benchmark Data on Liquid Fire Suppressants

Authors: C. Presser, B. Johnson, C.T. Avedisian (Cornell University), G. Papadopoulos (Dantec Dynamics), J. Hewson (Sandia National Laboratory), D. Keyser (NavAir), and P. Disimile and J. Tucker (46th Air Force Test Wing)

CSTL Program: Environmental Technologies and Services

Abstract: The new generation of non-ozone-depleting Halon alternatives include chemical suppressants that have high boiling point temperatures (i.e., Tb > 330 K) and exist in liquid phase under high-pressure release or in ambient conditions. Release of these agents in a confined cluttered space, results in the dispersal of droplets that either travel along ballistic trajectories, move with the convecting flow, or impact upon nearby solid obstacles. Therefore, an accurate representation of droplet transport is crucial for the numerical modeling of fire suppression in obstructed spaces of aircraft dry bays and nacelles using these agents. To better understand the physics of droplet transport around and behind solid objects, an experimental arrangement was set up to impose controlled grid-generated turbulence on the air stream (see Fig. 1). Experimental results from this facility provide new experimental data for a well-characterized, homogenous droplet-laden turbulent flow field around prescribed obstacles to provide data for flow model validation. Results are obtained using particle image velocimetry, phase Doppler interferometry, and visualization techniques. The liquid agents considered in the investigation were water, and two 3MTM fire protection fluorocarbons HFE-7100 (with a boiling point of 334 K) and HFE-7000 (with a boiling point of 307 K).

Purpose: Develop a parametric data set to guide and validate the VULCAN computational fluid dynamics fire physics code for spray-clutter interactive environments, under current development at Sandia National Laboratories.

Major Accomplishments: Phase Doppler measurements was used to obtain droplet size and velocity distributions in a droplet-laden homogenous turbulent flow field around a horizontal, cylindrical obstacle (see Fig. 1). Spatial profiles upstream and downstream of the 32 mm diameter cylinder (along the centerline and at off axis positions of 5 mm, 10 mm, 15 mm, and 20 mm) were completed of the droplet size and velocity distributions, and droplet number density, for HFE7000, HFE 7100, and water. Results were also obtained for water with the cylinder heated to 423 K. These measurements are valuable in evaluating the effects of different physical properties of the agent on droplet transport, and for elucidation of droplet size effects on impact and coating of the cylinder surface, rebound into the free stream, vaporization near the heated cylinder, and entrainment behind the cylinder. An atomizer, forming a 60 degree solid-cone spray upstream of the cylinder with a higher concentration of droplets in the center of the spray, was used in order to direct more liquid axially toward the cylinder. We also completed spatial profiles across the entire spray at 20 mm downstream of the atomizer and 50 mm upstream of the cylinder to provide initial conditions for subsequent simulations by Sandia, using the Vulcan fire code. The results (see Fig. 2) indicated that both HFE7000 and HFE7100 vaporized readily without any droplet accumulation and dripping from the cylinder, as was not the case for water. Droplet size is correlated with liquid boiling point, as indicated by the size distributions presented in Fig. 2. Downstream in the wake region of the cylinder, a distribution of smaller size droplets (generally, of less than 30 μm) is entrained in the recirculation zone. Comparison of results for the unheated and heated cylinder with water found that near the heated cylinder surface, droplet vaporization results in smaller mean droplet sizes, relative to the unheated case.

Impact: Results will establish correlation of the agent/spray properties, agent atomization methods, and agent dispersion effectiveness that will enable (in fire modeling and scale-up to intermediate- and full-scale testing) optimization of fire suppression performance of misted liquid systems.

Future Plans: This is the final year of participation in the Next Generation Program on Fire Suppression. It is expected that our results will be used to provide critical input and validation data for the Vulcan fire modeling efforts underway at Sandia National Laboratory. These results will also provide critically needed data to enable scale-up to intermediate- and full-scale testing that is currently underway for this program, and to optimize the fire suppression performance of misted liquid systems.

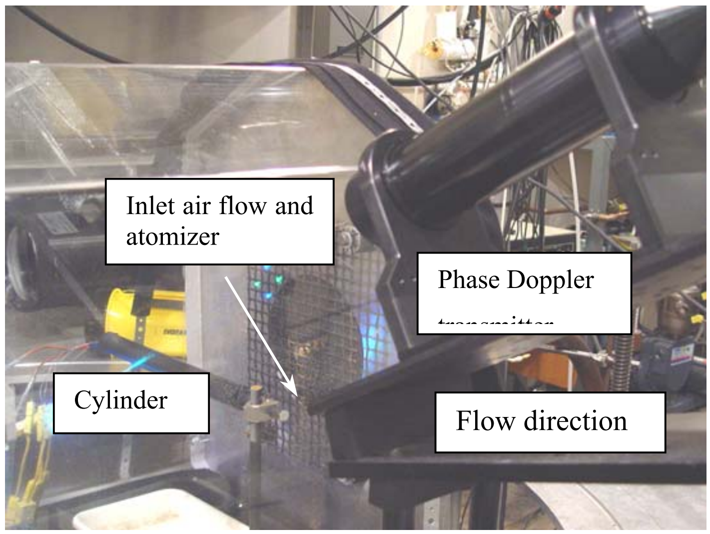


Fig. 1 Experimental arrangement for droplet size and velocity measurements during liquid spray transport over a cylinder that serves as an obstruction.

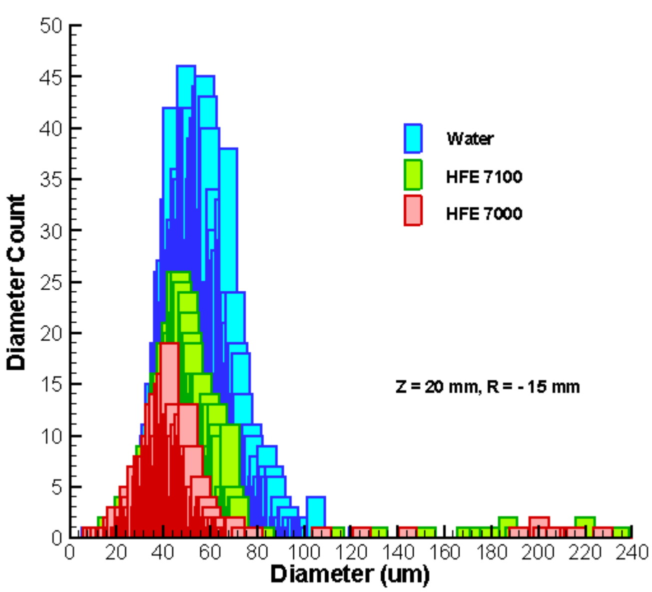


Fig. 2 Comparison of the size distribution for the three fire suppression agents at a particular spatial location in the spray upstream of the cylinder. Droplet sizes are larger for liquids with higher boiling points.

Standards for Raman Spectroscopy

Authors: *W.S. Hurst, S.J. Choquette (839), E.S. Etz (837), J. Maslar*

CSTL Program: Industrial and Analytical Instruments and Services

Abstract: This project critically evaluates existing approaches and develops new methods and associated standards that will provide for calibration of the intensity of Raman spectral data. Intensity calibration is needed to make process-control Raman measurements "instrument-independent", to enable analysis of spectral data for unknown mixtures, and to quantify instrument performance and stability as needed by US industries and by regulatory agencies such as the FDA. NIST is developing a series of fluorescent glasses that will become available as Standard Reference Materials (SRMs) that will provide instrument calibration. SRM 2241, a glass suitable for use with laser excitation at 785 nm, was made available last year. A new fluorescent glass with stable properties suitable for use with laser excitation at 532 nm, SRM 2242, will be available in early FY 04. SRM 2243, for 488 nm and 514 nm laser excitation, is under development and expected to be available in later FY 04.

Purpose: Raman spectroscopy is now finding its place in the industrial environment for process measurements and quality control. The lack of accepted practices, standards and spectral libraries has been a main obstacle to the acceptance of Raman in industrial settings and is a barrier to its use in the regulated industries. Intensity calibration of Raman spectra can be accomplished using white light sources, but this procedure requires expensive equipment, has a source with a limited lifetime, and provides a radiation source that is spatially different from the Raman process. These limitations can be avoided by using fluorescent glass artifacts of known relative irradiance. NIST will develop glasses for intensity calibration for use with popular laser excitation wavelengths that will be available as a set of SRMs traceable to NIST primary radiometric standards. Contact with the Raman community of major chemical industries, instrument manufacturers, regulatory agencies, and initiatives adopted by the ASTM E13.08 Subcommittee on Raman Standards will be maintained so that methods, standards, and techniques developed by NIST are widely accepted by the industry.

Major Accomplishments: A manganese-oxide bearing glass with broad-band fluorescent emission suitable for use with 532 nm laser excitation has been developed and characterized using three different commercial Raman spectrometers. It will shortly be issued as SRM 2242, which supplies the glass artifact along with a curve expressing its relative irradiance as a function of the Raman shift in wavenumbers. A new fluorophore and glass matrix composition for use with 488 nm and 514 nm excitation has been developed. This glass is stable and has suitable broad-band spectral response; however, work is ongoing to improve its resistance to laser bleaching.

Impact: This program is providing industry with an inexpensive and easily implemented means for calibration of the Raman spectral intensity. NIST standards will promote the acceptance of Raman spectroscopy as a tool for process control in the chemical and pharmaceutical industries and will provide a means for instrument qualification as required by regulatory agencies such as the FDA.

Future Plans: NIST work in Division 836 on SRM 2242 as an intensity standard for excitation at 532 nm has been completed; final data analysis by NIST's Statistical Engineering Division is needed to specify the associated uncertainty of this SRM before it is issued. A fluorescent glass, suitable for use at 488 nm and 514 nm, has been examined by members of the ASTM E13.08 for user advice on the magnitude of the intensity response, in order to establish the final fluorophore concentration. While the final fluorophore concentration has been determined, additional NIST work is needed to minimize laser-bleaching effects. The spectral response will then be characterized and made available as SRM 2243 in FY04. In response to requests by members of ASTM E13.08 for NIST to include in its suite of materials for intensity calibration one for use at 633 nm, NIST will develop and complete a SRM for 633 nm in FY04 and FY05. Characterization of heterogeneous materials as encountered in biological and semiconductor work has led to the development of Raman imaging systems and, within the last two years, of a new subcommittee ASTM E13.10 that is concerned with the specific set of requirements for calibration that is needed for imaging systems. NIST is participating in this subcommittee; however, work in this area would require a new programmatic effort by NIST.

Absorption Coefficient Measurements of Aerosol Particle Agglomerates

Authors: C. Presser, J. Conny (837), and A. Nazarian

CSTL Program: Environmental Technologies and Services

Abstract: Greenhouse effects associated with climate change may be influenced strongly by the chemical and physical properties of aerosol particles, i.e., particulate matter (PM), in the atmosphere. Currently, the largest uncertainty in predicting the temperature of the Earth's surface is poor knowledge of the optical properties of atmospheric aerosols, such as atmospheric soot and cloud condensation nuclei. Although a variety of methods are used to measure atmospheric aerosol elemental carbon (EC) mass, those based on thermal-optical analysis (TOA) are the most widely used. TOA technology is deceptively simple, but is based on poorly understood, complex physical and chemical mechanisms. Current 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. To address these issues, we have developed a new approach that will combine a laser-driven thermal reactor (LDTR) capability, an acoustic levitator, and Stokes/anti-Stokes Raman spectroscopy to provide a well-controlled thermal environment for non-intrusive determination of thermal-physical and chemical-kinetics properties of selected PM (e.g., combustion-generated soot).

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

Major Accomplishments: LDTR measurements were completed to determine the effect of carbon shape and size on its absorption characteristics. Results were obtained for a spherical and flat/disk shape compacted agglomeration of particles. This information is important for determination of real-world particle characteristics where the surface is not always spherical and well characterized by theory. Measurements were carried out for different average particle temperatures, up to 1200 K, to determine the heat transfer characteristics of quartz fiber filters (QF) that were cleaned and baked. These QF's serve as a substrate during collection of particulate matter. It was determined that the material's low thermal conductivity, the data obtained from a direct laser heating approach is more accurate and reliable than that from a second approach which is based on the heating rate. Absorption coefficient results were obtained from clean filters, and for filters exposed to laboratory air particles and soot at different sample temperatures (from ambient to 1180 K) and gas pressures (at 75 Torr and 750 Torr). An example of the absorption coefficient at 300 K is presented in Fig. 1. It was observed that the absorption coefficient increased with temperature for the clean filter, whereas the absorption coefficient decreased for the filter exposed to laboratory air particles and soot.

Significant progress was made in integrating the acoustic levitator and Raman spectroscopy diagnostics with the LDTR. New reactor copper spheres were designed and fabricated to allow for levitation of soot particles inside the sphere, and to provide optical access for the Raman measurements (see Fig. 2). Soot levitation was performed successfully to demonstrate the proof of the design concept.

Impact: Determination of the optical absorption characteristics of aerosol particulates with greater accuracy than current techniques can potentially 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 unknown.

Future Plans: We plan to continue developing this technique, and to use it 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 multicomponent 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.

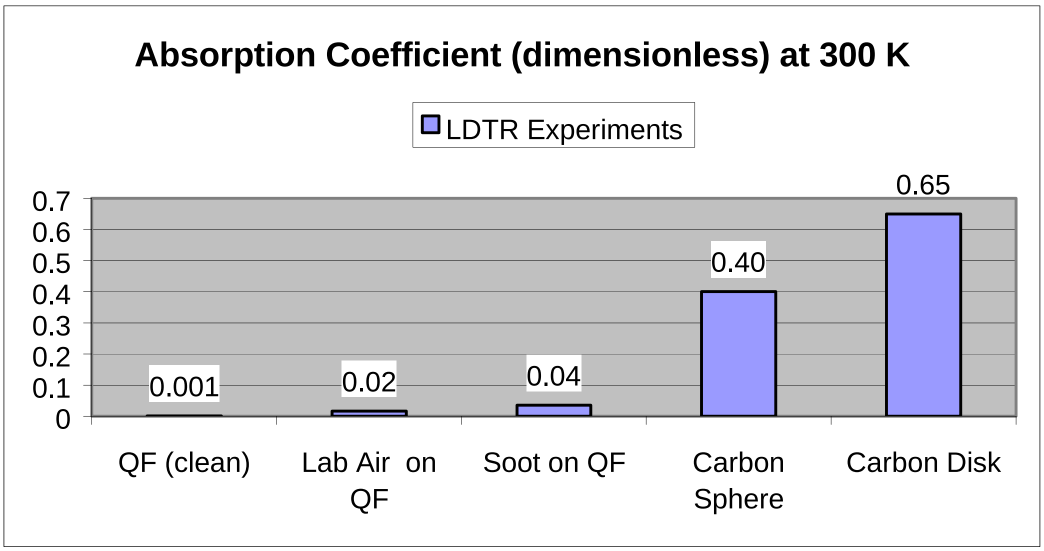


Fig. 1. Comparison of the absorption coefficient of different particles on a quartz filter, as measured using the laser driven thermal reactor.

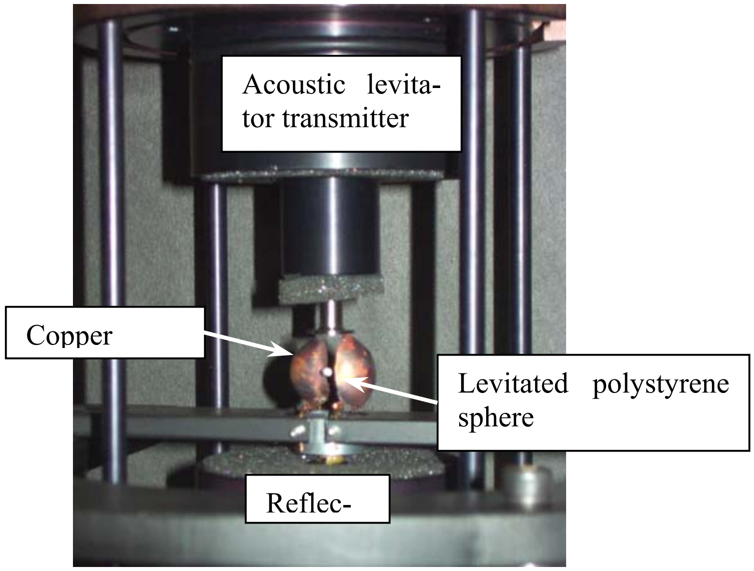


Fig. 2. Modified acoustic levitator that will be used to determine the absorption coefficient of particles without the influence of any substrate.

Non-Contact Free Carrier Density Measurements for Compound Semiconductors

Authors: J. E. Maslar and W. S. Hurst

CSTL Program: Microelectronics

Abstract: Transport of free electrical 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 material 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.

Purpose: Facilitate the development of a non-contact, spatially-resolved measurement of majority carrier concentration and mobility in the compound semiconductors comprising optoelectronic devices by establishing the accuracy and precision of Raman spectroscopic determination of these properties for a given material, set of measurement conditions, and Raman spectral model.

Major Accomplishments: Materials properties of different semiconductor materials can vary greatly. This often necessitates the use of different Raman spectroscopic systems when investigating different materials. A generally useful classification is based on the magnitude of the fundamental direct band gap of the material, a value which varies from about 0.36 eV for InAs to about 6.2 eV for AlN. Initial aspects of this investigation have focussed 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, AlN and AlGaN, obtained from various collaborators. For the narrow band gap, Sb-based materials, a near-IR Raman system was designed and assembled. This included evaluation and selection of a suitable solid state array detector, spectrograph gratings, Rayleigh scatter rejection filters, and lenses. For the wide band gap, N-based materials, a visible Raman microprobe system was designed and assembled. This included evaluation and selection of an optical microscope (and associated optics) and design of an appropriate optical interface between the microscope and spectrograph.

For determination of carrier densities, Raman spectra of n-type doped GaSb, p-type GaSb, n-type GaInAsSb, and n-type GaN were recorded. Modeling of the Raman spectra from the different materials also requires different spectral models. The spectral models for the Sb-based materials are based on a zinc blend crystal structure and account for conduction band non-parabolicity, absorption of excitation radiation, and included multiple carrier types (due to multiple conduction band minima being occupied). The computer code for modeling the Sb-based materials has been written and all n-type Sb-based material spectra we have obtained have been fit, see Fig. 1. These results have been compared to electrical measurements. From this comparison, it was determined that more sophisticated spectral models should be developed. The spectral models for the N-based materials are based on a wurtzite crystal structure and do not need to account for absorption or multiple carrier types. Results from the n-type GaSb and n-type GaInAsSb investigations were presented as oral papers at the 2003 Electronic Materials Conference (June 2003) and at the Fifteenth American Conference on Crystal Growth and Epitaxy (July 2003).

Impact: This project should facilitate the utilization of Raman spectroscopy for spatially resolved off-line characterization as well as process monitoring and control during film growth and etch processing. Future users will be able to determine the expected accuracy and precision for a given material, set of measurement conditions, and Raman spectral model.

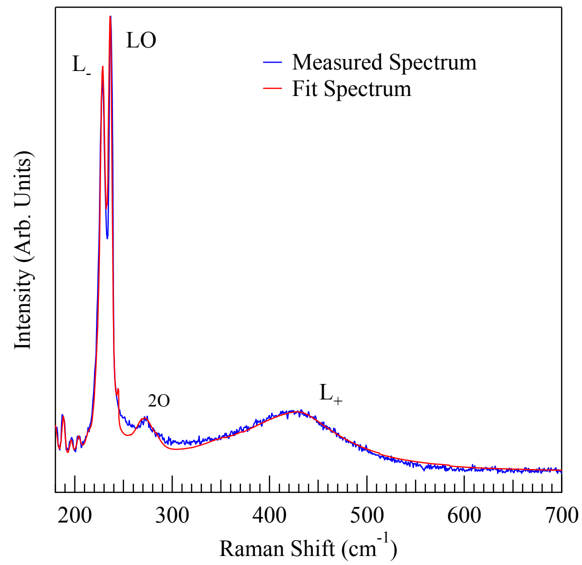


Fig. 1. The measured Raman spectrum for n-type GaSb. Fitting the data with a Raman spectral model results in a determination of carrier concentration of about 6×10^{18} cm^{-3}.

Future Plans: The first objective is to develop and benchmark more sophisticated spectral models in collaboration with NIST's Semiconductor Electronics Division 812 and Atomic Physics Division 842. Development of such models will also facilitate investigation of p-type films and alloy semiconductors. Another objective is the development of two dimensional analysis capabilities so that film uniformity can be examined. Also, doped AlGaN alloys are to be investigated. Finally, characterization of AlGaN/GaN high electron mobility transistor structures will be addressed. Results will be disseminated via publications and presentations.

Thermophysical Properties of Gases used in Semiconductor Processing

Authors: J. J. Hurly, K.A. Gillis, and M.R. Moldover

CSTL Program: Microelectronics

Abstract: CSTL responds to the expressed needs of the US semiconductor industries for gas property data by measuring the thermophysical properties of semiconductor process gases. 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 process gases, "surrogate" gases, and the binary mixtures of process and carrier gases of highest priority. They also established targets for the accuracy of the thermophysical property data that are needed to model manufacturing processes and to control the process quality. 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 Fig 1.) As results are acquired, NIST disseminates them via the internet at the URL http://properties.nist.gov/semiprop (Fig. 2). 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. The diffusion coefficients for gaseous mixtures of process gases and carrier gases will also be included.

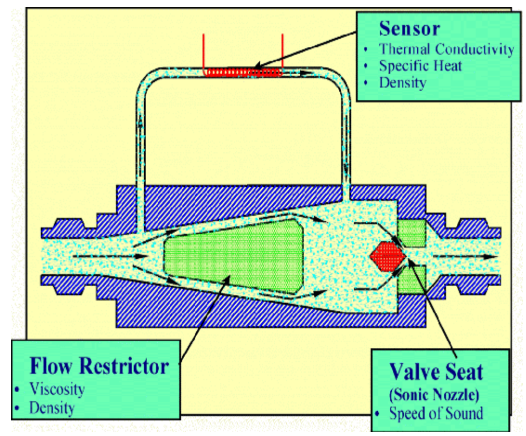


Fig. 1. Components of a generic mass flow controller (MFC) and the thermophysical properties required to model them.

Accomplishments and Impact: The Greenspan viscometer was installed in a facility for handling hazard ous gases. (See Figure 3.) Software was developed to allow safe, automated, remote operation of the viscometer.

By the end of FY03, we had used a Greenspan acoustic viscometer to measure the viscosity of 9 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. From the virial coefficients, we developed an equation of state that predicts the gas's densities to within 0.1 %.

During FY03, the theory of the Greenspan acoustic viscometer was completed, validated, and published. Using this theory, the viscosity results for five test gases agreed to within ±0.5 % with reference data.

Table 1. Gases and Conditions for Viscosity Data.

1. *Ga*	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

The results of this research have been disseminated by nine publications in professional journals and by a series of talks at professional meetings. During FY03, three new publications were submitted to archival journals and two talks were presented. 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: During FY04, we shall install a new spherical resonator and measure the speed out 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 install a corrosion-resistant Greenspan viscometer and measure the viscosity of two hazardous process gases: HBr and NO. No viscosity data exist for these gases; thus, the NIST results will decrease the uncertainty of the viscosity from an estimated 10 % to approximately 0.5 %.

We will complete the modeling of an acoustic resonator optimized to measure the thermal conductivity of process gases.

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

Figure 3. The Greenspan viscometer being installed in the new hazardous gases facility.

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	$B(T)$ $cm^3 \cdot mol^{-1}$	dB/dT $cm^3 \cdot mol^{-1} \cdot T^{-1}$	$C(T)$ $cm^6 \cdot mol^{-2}$	dC/dT $cm^6 \cdot mol^{-2} \cdot T^{-1}$	λ mW/(m·K)	η µPa·
Estimated Uncertainty	1%/0.1%	1%	Gas densities are calculated to better than 0.1% over the temperature and pressure ranges of the reference.				10%	10%
Reference	[4]/[5]	[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	28924191	5.2	14.1
220	12.66	0.95	-1631.6	4600.8	-2291407	22949084	5.4	14.4
225	12.78	1.53	-1532.2	4252.9	-1829413	18345717	5.6	14.6

Fig. 2. Sample Web Page from database located at the URL Hhttp://properties.nist.gov/semiprop/H

Atomic Standard of Pressure

Authors: M. Moldover, J. Schmidt, K. Szalewicz (U. Delaware), Y. Wang (811)

CSTL Program: Technologies for Future Measurements and Standards

Abstract: CSTL researchers are developing a novel primary standard for pressure in the range 0.3 MPa to 5 MPa. The new standard will determine the pressure $p(\varepsilon,T)$ by measuring and calculating the dielectric constant $\varepsilon(p,T)$ of helium with extraordinary accuracy. The uncertainties from electrical and temperature measurements will be smaller than the uncertainty of existing pressure standards (piston gages).

Purposes: **(1)** To replace artifact-based pressure standards with a standard based on calculable properties of a pure substance: $\varepsilon(p,T)$ of helium gas and, **(2)** to reduce the uncertainty of pressure standards in the range 300 kPa to 5 MPa. Below 300 kPa, the primary pressure standard at NIST is a 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 against 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. Piston-cylinder sets exhibit a poorly-understood specie and gas flow dependencies. Thus, the extrapolation is not fully trusted and it cannot be checked with existing technologies. When $\varepsilon(p,T)$ of helium becomes the pressure standard, it will be possible to test models of piston-cylinder sets and to reduce their uncertainty.

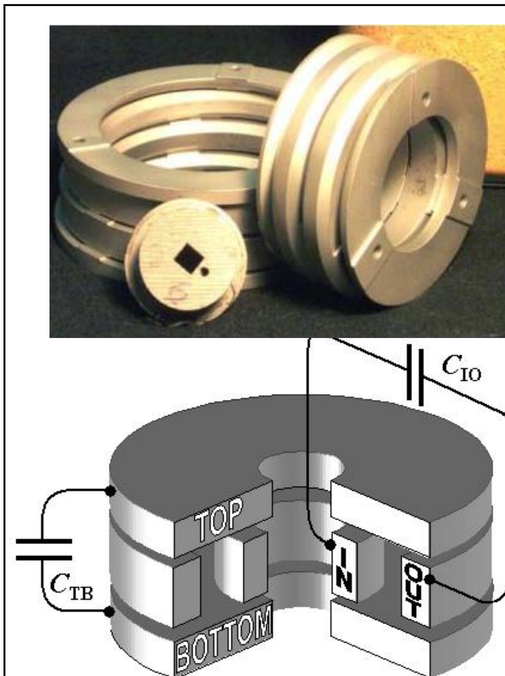

Figure 1. Section of cross capacitor and components.

Accomplishments: Dielectric constant measurements are being improved by drawing on NIST's expertise in electrical metrology. Using that expertise, we developed a novel, doughnut-shaped, four-electrode, cross capacitor. (See Fig. 1.) In comparison with conventional capacitors, cross capacitors are more stable and less subject to surface contamination (oxides, adsorbed water, or films of oil). Toroidal capacitors have an additional advantage; there are no "end effects" to complicate measurements. During FY02/03, a toroidal cross capacitor and a rod-shaped cross capacitor were used to measure the dielectric constant of helium in the range 0 to 7 MPa. The measured values of $\varepsilon(p,T)$ from the cross capacitors of differing designs were consistent with the theoretical values and with each other within an uncertainty of 2×10^{-7} which corresponds to a relative pressure uncertainty of 5×10^{-5} which is approximately an order of magnitude larger than current pressure standard uncertainties.

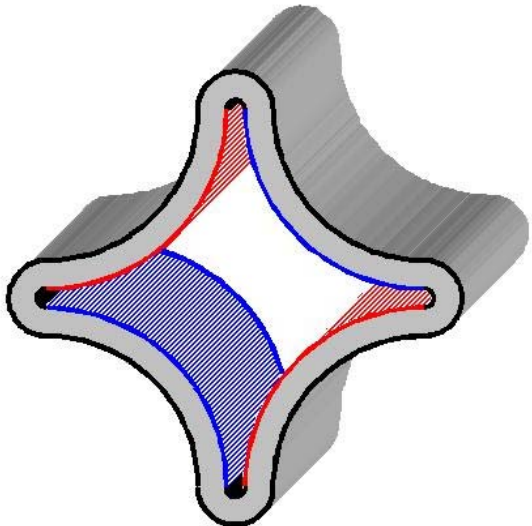

Figure 2. Sketch of single crystal sapphire cross capacitor. Thin-film electrodes are colored blue and red. The prototype is 25 cm long and 2 cm across the largest "diameter."

To reduce the uncertainty a factor of ten, we are simultaneously attacking the problem on four fronts:

(1) improve the theory for $\varepsilon(p,T)$ and the theory for the virial coefficients of helium,

(2) manufacture cross capacitors with greater stability and larger capacitances,

(3) obtain a more accurate capacitance bridge for measuring $\varepsilon(p,T)$ at audio frequencies,

(4) measure $\varepsilon(p,T)$ with high resolution at microwave frequencies.

The theory for $\varepsilon(p,T)$ is being advanced at the University of Delaware. A concept for a more stable cross capacitor is shown in Figure 2. This capacitor is made from a single, long, sapphire crystal. The crystal is edge-grown, with a hollow, star-shaped cross section. It has four surfaces that are coated with thin electrodes. We expect that the single-crystal sapphire capacitor will be more stable than conventional cross capacitors assembled from many metal and insulating parts.

To advance capacitance bridge technology an order of magnitude, NIST has let a SBIR contract to a bridge manufacturer. In parallel, the Electricity Division of NIST is developing the technology to test such a bridge when it is delivered. It is not certain that capacitance bridges can achieve the desired performance at a reasonable price. Thus, CSTL is exploring the alternative of making very accurate measurements of $\varepsilon(p,T)$ of helium at microwave frequencies. Our approach uses quasi-spherical microwave cavities. This concept grew out of CSTL's long experience in developing and using of spherical cavities for acoustic thermometry.

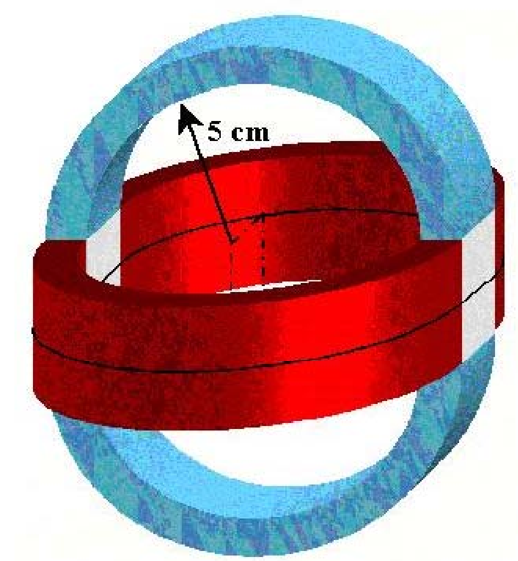

Fig. 3. Quasi-Spherical Microwave Cavity. The cavity is assembled from hollow, copper, quasi-hemispheres. Each quasi-hemisphere has the shape of two quadrants of a sphere (radius = 5 cm) with 0.01 cm wide cylindrical extensions (exaggerated in the sketch). The extensions split degenerate microwave frequencies.

Impacts: If successful, this program will revolutionize pressure standards and greatly improve capacitance bridges. Already, CSTL has used cross capacitors to measure $\varepsilon(p,T)$ of the primary constituents of natural gas including methane, ethane, propane, nitrogen, carbon dioxide, and argon. The measurements span the 0ºC to 50ºC temperature range and extend to 7 MPa. In this range, they are more accurate than any previous measurements and provide reference data for use in metering natural gas.