I. Process Measurements Division

James R. Whetstone, Chief
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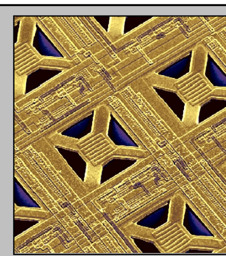
A. Division Overview

Mission:

The Process Measurements Division develops and maintains technical competencies and capabilities in support of CSTL programs. The Division pursues research efforts in measurement science as the basis to enhance measurement standards and services, measurement techniques, recommended practices, sensing technology, instrumentation, and mathematical models required for analysis, control, and optimization of industrial processes. Improvement and dissemination of national measurement standards for temperature, fluid flow, air speed, pressure and vacuum, humidity, liquid density and volumetric measurements are core Division responsibilities. The Division's research seeks fundamental understanding of, and generates key data pertinent to, chemical process technology. These efforts include the development and validation of data-predictive computational tools and correlations, computer simulations of processing operations, and provision of requisite chemical, physical, physical property, and engineering data.



Process Measurements

J. Whetstone, Chief

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

Organizational Structure:

The Division, which contains the equivalent of 71 full-time staff members representing a range of technical competencies, supports seven of the 12 CSTL program areas. The Division is organized to support the evolution and strengthening of these competencies. It is comprised of six groups with the following mission statements:

Fluid Flow Group

- Establish, maintain, and disseminate the reference standards needed by U.S. industry for fluid flow rate and liquid quantity measurements,
- Conduct research to advance fluid transfer measurement science,
- Establish and maintain international comparability in fluid flow rate and fluid quantity measurements, and
- Interact with industrial counterparts and standards committees to provide expertise and assistance to U.S. industry and other government agencies in advancing fluid transfer technology.

Process Sensing Group

- Develop, validate, and apply state-of-the-art measurement techniques and sensors for process optimization and control of plasma reactors used in semiconductor manufacturing,

Process Measurements Division Activities In Support of CSTL Program Directions in:

- **Semiconductor Metrology**
- **Process Metrology**
- **Chemical and Biochemical Sensing**
- **Physical Property Data,**
- **Chemical and Biochemical Data, and**
- **International Measurement Standards**

Competency Areas

- Fluid Mechanics
- Flow Measurements
- Computation Fluid Dynamics
- Chemical Process Modeling
- Thermometry
- Piston Gauges and Manometry
- Vacuum Measurements and Standards
- Humidity Measurements and Standards
- Raman Spectroscopies
- Absorption Spectroscopies
- Cavity Ring Down Spectroscopy
- Surface Plasmon Resonance Spectroscopy
- Optical Particle Characterization and Sizing
- Spray Systems
- Laser Diagnostic Techniques
- Plasma Diagnostic Techniques
- MEMS and Solid State Chemical Sensing
- Microfluidic Devices
- Acoustic Measurements
- Physical Properties of Fluids

- Develop scientific and technological underpinning for application-tunable, low-cost, micromachined gas sensor arrays to meet measurement needs in process control, emissions monitoring, and hazardous gas detection, and
- Provide scientific and technological foundation for the use of ultrathin organic films in sensing and diagnostic applications in chemical and biochemical process monitoring and health care.

Thermometry Group

- Realize, maintain, and disseminate the national standards for:
  - temperature, (the International Temperature Scale of 1990, over the range 0.65 K to 1235 K) and
  - humidity, (moisture in air: 5 nmol/mol to 75 mmol/mol),
- Perform research on developing or improving primary standards and measurements for temperature and humidity,
- Develop methods and devices to assist user groups in the assessment and enhancement of the accuracy of their measurements of temperature and humidity, and
- Co-ordinate and participate in international comparisons of realizations of the International Temperature Scale of 1990 and of national standards of humidity.

Pressure and Vacuum Group

- Develop and maintain primary pressure, vacuum, and low gas flow standards and disseminate the measurement capability to U.S. industry,
- Advance pressure, vacuum, and low gas flow measurement science:
  - Conduct research to develop measurement standards and techniques to meet U. S. industry requirements,
  - Perform benchmark measurements of material properties and investigate fundamental physics of industrially important phenomena which require state-of-the-art pressure, vacuum, and low flow measurements, and
  - Collaborate with industry and academia in the development of new instrumentation to improve industrial process control or for use in critical scientific measurements.

Thermal and Reactive Processes Group

Develop advanced mathematical models, advanced measurement techniques, standard measurement practices and performance data for analysis, control, standardization, and optimization of key industrial processes; current focus is on:

- liquid atomization and spray combustion, and
- chemical vapor deposition.

Fluid Science Group

- Develops and applies state-of-the-art techniques based on acoustics and other novel approaches for measuring the thermodynamic and transport properties of fluids and fluid mixtures, including semiconductor process gases and components of natural gas.
- Performs research on next-generation primary standards for temperature, pressure, and low flow rate in gases.

Programs:

The Division pursues measurement science research and development projects and measurement standards dissemination activities that contribute to accomplishing CSTL programs. In several cases the breadth of potential applications of our research work is such that project results impact several CSTL program areas. Brief description of our activities follow. Summaries of FY 2000 program accomplishments are given in the 23 technical articles that follow this overview.

Semiconductor Metrology

CSTL's Semiconductor Metrology program contributes to the NIST National Semiconductor Metrology Program (NSMP) that is managed by the Office of Microelectronic Programs (OMP) of the NIST Electrical and Electronic Laboratory. CSTL competencies in several areas contribute to metrology developments need 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 efforts include:

- development of thermocouple technology for control of thermal processing equipment, including thin film/wire instrumented silicon wafer technology to support in-situ calibration of radiometric devices used for control of rapid thermal processing (RTP) systems,
- improved standards and data for mass flow controllers include improvement in low-range gas flow standards and provision of transport

property data for chemically reactive process gases,
- develop quantitative measurement capability to enable a real-time, *in-situ* semiconductor process-control based on optical diagnostic and improved flow calibration techniques,
- models for contamination control in thermal CVD processes,
- methods to determine electrical, physical, and chemical properties of plasmas used for etching and reaction chamber cleaning processes, and
- very low-level water vapor measurements and standards for contamination control in process gases.

In some of these efforts, 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. Because processing systems are complex, with strongly coupled chemistry and mass-transport and, in the case of plasma reactors, complex electrical interactions, reference reactors are subject to extensive modeling and validation efforts as an integral part of the measurement support activity. These models and supporting data play a critical role in the Semiconductor Industry Association's (SIA) National Technology Roadmap for Semiconductors (ITRS). In fact, modeling is specifically identified not only as a "crosscutting technology," but as "pervading all crosscuts." Our program in this area, partially supported by the NSMP, seeks to develop and validate benchmark chemical mechanisms and supporting thermochemical and kinetic data, for equipment and process design and control.

Program Highlights

Many of the processes used in semiconductor manufacturing are inherently chemical in nature. The reactants are introduced in the gas phase resulting in the wide use mass flow controllers (MFCs) to meter the appropriate quantity of material to the reaction vessel. Division efforts are directed toward improving both the flow standards used in industry for **MFC calibration and thermophysical property data** for a range of process gases. MFCs are normally calibrated with benign surrogate gases, e.g., N_2, CF_4, SF_6, and C_2F_6, but are then are used to deliver reactive process gases, e.g., Cl_2, HBr, BCl_3, WF_6, using 'gas factors' to adjust for gas property differences. Application of 'gas factors' to MFC calibrations often thought to be the source of significant errors in the quantity of gas delivered to the process.

The semiconductor manufacturing industry needs higher accuracy than currently available in measuring the temperature of silicon wafers during **Rapid Thermal Processing** to achieve goals in product quality and device performance. Consequently, the industry roadmap now requires an uncertainty of ≤ 2 °C at 1000 °C for RTP for the next generation of wafer patterning. Radiation thermometers are used in RTP but the uncertainty in measurements made with them is unacceptably large when the thermometers are calibrated against blackbodies.

We are developing improved calibration techniques for the light-pipe radiation thermometers (LPRTs) used to control RTP systems. Si wafers instrumented with combinations of stable thin-film and Pt/Pd wire thermocouples (TCs) minimize errors from heat transfer that would be present for other types of temperature sensors. In FY 2000 we increased the operating temperature of our TC-instrumented calibration wafers to 1000 °C to meet the upper temperature requirement seen in industrial operation while continuing to improve our understanding of sources of measurement uncertainty. Additionally, we have investigated the effect of the operating temperature of the light pipe portion of the LPRT on the indicated temperature and have found that the radiation surroundings can have significantly effects.

Our technology transfer activities have continued and expanded. Our cooperative project with SEMATECH, University of Texas, and Sensarray Inc. has included the design, fabrication, testing, calibration, and delivery of two thin-film calibration wafers for testing in their unique RTP instrumentation test bed. Other industrial and academic technical transfer activities have included providing thin-film calibration wafers to Applied Materials and Vortek Industries for test and evaluation in commercial RTP tools. Additionally, the NIST patent on the "Temperature calibration wafer for rapid thermal processing using thin-film thermocouple" #6,037,645 was issued Mar. 14, 2000 and licensed to Watlow Gordon Inc. for commercial production of the thin-film/wire thermocouple instrumented wafer technology.

Particle formation from gas phase reactants in CVD reactors is a contamination source not well described by **CVD process simulation models** due to inadequate of particle formation mechanisms in these complex systems. The Division is developing models describing silicon deposition that include gas-phase nucleation, condensation, and growth of particles in a rotating disk CVD reactor. Particle scattering intensities were measured experimentally via laser light scattering and were compared with those predicted by the semi-empirical NIST microcontamination model and found to be in close agreement. This model contains two empirical parameters relating thermophoretic force and condensational sticking coefficient. Proper choice of these parameters results in the excellent agreement between experimental results and model prediction. In the coming year we will extend the modeling effort to a more physically based particle formation mechanism, determine gas phase concentrations near the particle layer, and begin looking at the effects of dopant gas influence on the system.

Our research activities in this program are described in Technical Reports 1 – 6.

Process Metrology

The Division contributes substantially to the CSTL Process Metrology Program. Our efforts include a broad range of research activities. A significant portion of these efforts maintains and advances national measurement standards for temperature, fluid flow, air speed, pressure and vacuum, humidity, liquid density and volumetric measurements. Several of our measurement science research projects address the development and demonstration of new approaches to the realization and effective dissemination of national measurement standards. The thrust of these efforts is the reduction of measurement uncertainty in the realization of national measurement standards. The expertise resulting form these efforts directly supports CSTL's International Measurement Standards Program in which U.S. national standards are compared with those maintained by other National Metrology Institutes (NMIs). The Division is responsible for all physical measurement standards provided by CSTL. Dissemination of and access to these national measurement standards is accomplished through our instrument calibration services. Therefore, several activities involve enhancing and disseminating national measurement standards to industry and other government agencies.

Dissemination of measurement standards in many cases provides the means to achieve process and quality control and equity in commerce because these ultimately depend on the accuracy of measurements. This generally requires calibration of instruments against, or use of procedures assuring traceability to reference standards. Therefore, measurement standards and calibration services are major Division activities. We provide support critical for temperature, humidity, fluid flow rate, pressure, vacuum, gaseous leak rate, liquid density and volume, and air speed measurements with almost 1000 standard tests and calibrations performed each year. The Division's commitment to provision of these services involves many facets:

- the establishment, maintenance, and improvement of the primary standards;
- continuing comparisons of these standards with those of other nations;
- development of suitable mechanisms for transferring the requisite measurement accuracy to customers in the field and in secondary calibration laboratories; and
- continual attention to calibration service efficiency and measurement quality.

The Division's efforts supporting CSTL's Process Metrology Program include:

- advances in flow measurement standards and new approaches to flow measurement methods,
- development of standard for low concentrations of water vapor in gases,
- high sensitivity optical detection methods based on evanescent wave cavity ring down spectroscopy,
- improving the accuracy of thermodynamic temperature measurements,
- standards for Raman spectroscopy,
- a new approach to primary pressure standards based on toroidal cross capacitors and high accuracy electrical measurements, and
- improvement in piston gauge pressure standards.

<u>Program Highlights</u>

We continue to improve **pressure measurement standards** both through advances in the more traditional piston gauge technology and through the development of new approaches to absolute pressure measurement. Piston gauge uncertainties are described by the uncertainty in their effective area. Recent advances in manufacturing technologies have reduced dimensional tolerances of pistons and cylinders the sub-micron level providing the opportunity to accurately dimension these components with nanometer resolution. We have taken advantage of a newly commissioned dimensioning system at the German national metrology institute, *Physikalisch-Technische Bundesanstalt*, which currently has the smallest measurement uncertainty of an NMI in these types of dimensional measurements. We sent our piston and cylinder components there for comprehensive dimensional determinations of. The roundness and straightness measurements obtained from PTB were compiled to form a three-dimensional grid structure and resulted in a relative uncertainty of the area of between three and four ppm at 20°C and at zero applied pressure. In FY2001, we plan extensive testing to quantify all uncertainty components and comparison the gauge with the ultrasonic interferometer manometer as well as with other reference piston gauges. In addition, the thermal expansion and pressure coefficients of the gauge will be quantified. We anticipate a reduction in the uncertainty of approximately four times that of our currently stated value. These developments may represent the ultimate precision obtainable with this technology.

An alternative approach to pressure standards continues through the measurement and calculation from first principles the dielectric constant of helium, $\varepsilon(p)$, with sufficient accuracy to make the pressure uncertainty obtained from existing standards (piston gages) significantly larger than the pressure uncertainty obtained from in $\varepsilon(p,T)$. Dielectric constant measurements are being improved by drawing on NIST's expertise in electrical metrology. With that expertise a novel, doughnut-shaped, four-electrode cross capacitor has been developed. For helium pressures up to 7 MPa, the cross capacitor concept was experimentally proven at the level of approximately $0.3\times10^{-6} \times\varepsilon(p)$. Further development of this approach may result in the ability to measure pressure at level approximately one of order of magnitude below our current capability. In addition to investigation as a potential pressure standard, the cross-capacitor system has been used to make reference-quality measurements of ε(p) for methane, nitrogen, carbon dioxide, argon, and helium at 50°C. This work also supports CSTL Chemical and Biochemical Data program.

Our research in this program is described in the Technical Reports 7 – 16.

Chemical and Biochemical Sensing

The Division has a significant effort supporting the CSTL Chemical and Biochemical Sensing Program tht involve research in the area of: micro-machined gas sensor arrays, diagnostic applications of self-assembled monolayers (SAMs), and measurements in micro-fluidic devices and structures. The chemical sensor research is collaborative with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory. The technology is based on NIST developed, and patented, 'micro-hotplate' arrays formed by silicon micro-machining. 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. The objectives of our effort are to develop the knowledge base required to optimize multi-species detection and quantitative analysis and to resolve generic device-processing issues that could limit commercial application. In FY 2000 we developed methods that significantly increase the sensitivity and stability of micro-hotplate chemical sensors. Sensitivity to methanol in air at the 10 ng/g level were demonstrated using a nanoparticle-based sensing material. In addition stable performance of the device was demonstrated over a 100-hour testing period. Also, nanophase, doped sensing oxides produce high sensitivities without the fouling effects that are often observed on metal catalyst-doped films. Technical Report 18 discusses these developments.

In the SAM's research effort, efforts are focused on alkanethiol monolayers, of the general formula $X(CH_2)_nSH$, self-assembled on the surfaces of noble metal substrates. These SAMs are robust, reproducibly prepared structures with highly tunable surface properties, and serve as a model system for the study of many sensing applications. An example is DNA microchip technology, which has potential application in the areas of disease detection, toxicology, forensics, industrial processing, and environmental monitoring. Our research currently is focused on the self-assembly of DNA monolayer films on surfaces and on their use as DNA probes. We have demonstrated the dependence of hybridization efficiency on target length and developed methods to develop near defect-free SAMs. These developments are discussed in Technical Report 19.

The Division's efforts in the the micro-fluidic device technology area is collaborative with CSTL's

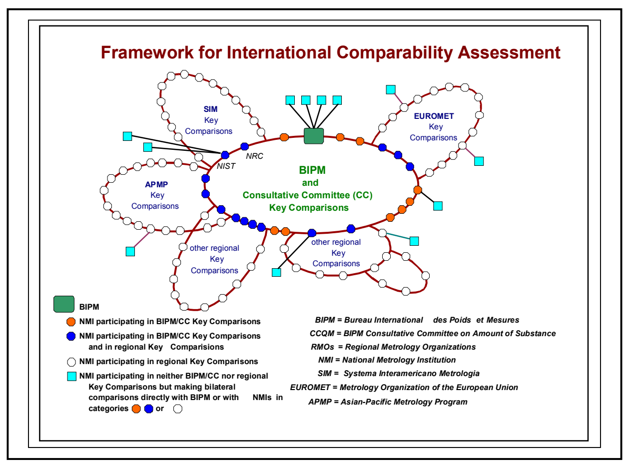
Analytical Chemistry Division. Research efforts are focussed on dynamic behavior, chemical selectivity, and detection in micro-channel structures. Although micro-fluidic, or so-called “lab-on-a-chip”, devices are currently receiving considerable attention and successful miniaturization of a broad range of chemical analysis techniques is impeded by poorly understood mechanisms that control their operation. Research efforts in this NIST competence project investigate the behavior of micro-channel structures formed in polymer substrates. Although miniaturized devices for DNA sequencing have recently become available commercially, the high cost of silicon-based devices will limit applications to a limited number of areas. Realization of the potential of micro-fluidic devices requires that manufacturing cost be significantly reduced. Polymer-based structures have this potential, but also present a number of challenges to their successful use. Although, micro-channels are easily formed in polymers, the movement of fluid through them reliably is still problematic, particularly using electro-osmotic flow (EOF) methods. EOF is simple and widely used but is adversely effected by micro-channel surface properties in these large surface-to-volume ratio structures. We have measured electroosmotic mobility and flow profiles in different plastic devices and developed methods of treating micro-channel surfaces in different plastics to provide device designers with greater operational reliability. Such fundamental data relating flow to surface properties will enable developers of this technology to tailor plastic microfluidic channels for specific applications.

Chemical and Biochemical Data

Division efforts in the Chemical and Biochemical program focus on development of benchmark experimental data for input and validation of multiphase combustion models in addition to development of methods for calibration of instruments and sensors and advanced diagnostic techniques. Computational Fluid Dynamic modeling is widely used by to design and optimize industrial combustion processes and systems. Although modeling can be cost-effective design tool, model validation is critical to success. In spray combustion data droplet field characteristics, flame structure, heat transfer, and particulate/gaseous reaction products and the interrelation with operating conditions are critical to the accuracy of a models predictive capabilities. This year a benchmark experimental database was released to our partners in industry and academia. A one-day workshop was held to further identify future needs for multiphase combustion data. A primary concern of both industry and the regulatory community is the issue of particulate matter entering the environment. The need for particulate matter standards was identified as a high priority area where NIST could make a significant impact. Technical report 20 discuss this topic is greater detail.

International Measurement Standards

As the National Measurement Institute of the U.S., NIST is responsible for comparison of U.S. national measurement standards with those of other nations. Such comparison efforts are performed under the auspices of the Committee International des Poids et Mesures (CIPM) and its various consultative committees. In addition, coordination of similar efforts with Regional Metrology Organization such as Sistemo Interamericano Metrologia (SIM) which includes the countries in the Americas are designed to extend the comparison efforts to as many participants as practicable.



Standards comparisons activities among NMIs are organized by the the respective Consultative Committees of the CIPM and initiated in selected NMIs which are then designated Pilot Laboratories. These Pilot Laboratories design and pre-test the transfer standards and test procedures; they arrange and schedule tests among participating NMIs; and they analyze data and report results.

In FY 2000 our efforts in this program have continue at a somewhat reduced level from previous years due to the completion of several activities. The following is a brief summary of these efforts.

Comparisons of Realizations of the International Temperature Scale of 1990 (ITS-90).

The Division is participating in four Key Comparisons (KC) of realizations of the ITS-90 organized by the CIPM Consultative Committee for Temperature (CCT). We are the pilot laboratory for KC 3 [83.8058 K (Ar triple point (TP)) to 933.473 K (Al freezing point (FP))] with 14 national laboratories plus Bureau International des Poids et Mesures (BIPM) participating. The measurements phase of the work has been completed and this year an exhaustive report has been written. The report will be finalized and submitted to the CCT for its acceptance in early FY 2001. Efforts in the remaining 3 Key Comparisons continues.

Expansion of KC3 with SIM is under discussion with interested NMIs of the Americas. NIST involvement in developing the procedures and protocols for this comparison is currently in the discussion phase due to the extensive experience gained from KC3. In the coming year the NMIs wishing to participate will be determined and a set of protocols and a transfer standard package developed. Technical Report 23 discusses these activities in more detail.

International Comparisons of Pressure and Vacuum Standards.

In FY00, the Pressure & Vacuum group participated in:

- six CCM Key comparisons spanning the range 10^{-6} Pa to 500 MPa,
- one bilateral comparison with the Czech Metrology Institute,
- two SIM comparisons from atmospheric pressure to 100 MPa, and
- one domestic comparison from atmospheric pressure to 1.4 MPa under NCSL-International.

NIST is piloting three Key comparisons, two of which completed the Draft A phase, and the third nearing completion of the measurement phase. For one SIM comparison, we discovered a transfer package shift necessitating a repeat of the comparison, while the results for the successful NIST-piloted comparison for the NCSL were presented at their annual meeting. For FY01, we will diminish our participation in the CCM Key comparisons as they conclude, while increasing our efforts in SIM and NCSL-International comparisons.

The BIPM/CIPM Working Group for Fluid Flow.

In the past year, the newly formed BIPM/CIPM Working Group for Fluid Flow (WGFF), chaired by G. E. Mattingly, has formed its strategy, structure, and schedules to attain its goal of…"providing governments and other parties with secure technical foundations for wider agreements related to international trade, commerce and regulatory affairs". The NMIs participating in the WGFF met for the first time in June 2000 to begin organizing a system of comparisons of national measurement standards for six areas:

flowrate measurements for:

- water
- hydrocarbon liquids,
- low-pressure air, and
- high-pressure natural gas,

and related measurement areas of:

- air speed and
- liquid volume.

Primary and secondary leadership roles in each area were assigned and accepted by respective NMIs. The initial WGFF tasks for the NMIs in each measurement area will be to review the Calibration and Measurement Capabilities (CMCs) of the other NMIs in that area and either accept or express reservations regarding quoted uncertainties. These reservations are then subsequently used to design and conduct Key Comparison (KC) tests that will confirm or refute the suspect uncertainties. Ultimately, when WGFF efforts for the acceptability of the CMCs and the results of the KCs confirm the equivalence of the flow standards in the world's NMIs are made public and available to all, via the internet, measurement-based, non-tariff trade barriers may be eliminated worldwide.

NIST has undertaken a primary role in low-pressure air and a secondary role in high-pressure natural gas. Technical Report 22 reviews these responsibilities in more detail.

Awards in FY 2000:

Gregory E. Poirier was selected as the NIST Sigma Xi Young Investigator of the Year 2000 acknowledging his groundbreaking studies of self-assembled monolayers using scanning tunneling microscopy.

Richard E. Cavicchi was recognized with the Department of Commerce Bronze Medal for his pioneering efforts in silicon micro-machined, thin-film sensor array technology for detection and measurement of gases.