

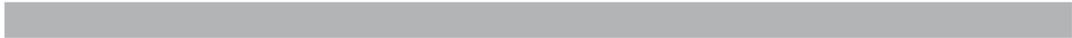
PROCESS METROLOGY PROGRAM

Device scaling has been the primary means by which the semiconductor industry has achieved unprecedented gains in productivity and performance quantified by Moore's Law. Until recently only modest changes in the materials used have been made. The industry was able to rely almost exclusively on the three most abundant elements on Earth — silicon, oxygen, and aluminum.

Recently, however, copper has been introduced for interconnect conductivity, replacing aluminum alloys. A variety of low-dielectric constant materials are being introduced to reduce parasitic capacitance, replacing silicon dioxide. As dimensions continue to shrink, the traditional silicon dioxide gate dielectric thickness has been reduced to the point where tunneling current has become significant and is compromising the performance of the transistors. This is requiring the introduction of higher dielectric constant materials. Initially the addition of nitrogen to the gate material is sufficient, but in the near future more exotic materials such as transition metal oxides, silicates, and aluminates will be required. As dimensions are reduced, gate depletion effects and dopant diffusion through the gate dielectric are limiting transistor performance. With the replacement of the traditional silicon dioxide/polysilicon gate stack processes with materials capable of supporting ever shrinking geometries, the task of the industry becomes more difficult. The overall task represented by the projects below reflects the need for analytical techniques with unparalleled spatial resolution, accuracy, robustness and ease of use.

Accurate metrology of process gases is essential for reproducible manufacture of semiconductor products. Critical physical parameters need to be measured on a wide variety of reactive and non-reactive process gases, allowing the accurate calibration of flow meters and residual gas analyzers. Water contamination at extremely low levels in process gases presents serious manufacturing difficulties. Accurate calibration of water vapor at extremely low vapor pressures is required.

Accurate metrology of process gases is essential for reproducible manufacture of semiconductor products and a wide variety of metrology issues emerge in plasma, chemical vapor, and rapid thermal processing steps used in semiconductor manufacture.



GAS PROPERTY DATA AND FLOW STANDARDS FOR IMPROVED GAS DELIVERY SYSTEMS

GOALS

NIST will measure the thermophysical properties of the gases used in semiconductor processing. The property data will improve the modeling of chemical vapor deposition and the calibration of mass flow controllers (MFCs). As the data are acquired, they will be posted to an online database.

NIST also will develop primary standards for gas flow in the range from 10^{-7} to 10^{-3} mol/s and transfer this flow measurement capability to the US semiconductor industry (10^{-6} mol/s \approx 1.3 standard cubic centimeters per minute (sccm)).

CUSTOMER NEEDS

The 2003 *International Technology Roadmap for Semiconductors* (ITRS) emphasizes that the grand challenge for front-end processes is “material limited device scaling.” The Modeling and Simulations section reinforces this theme: “*Modeling and simulation tools in equipment, process, device, package, patterning, and interconnect are only as good as the input materials parameters. In many cases, these parameters are not known. Databases ... are needed.*” Meeting this challenge will require improvements in MFCs for the deposition and etching of diverse new materials. Thermal MFCs meter a wide variety of toxic, flammable, and corrosive gases over a large range of flow rates. Elements necessary for improved MFCs will be accurate models of gas properties and reliable physical standards for gas flow.

Participants at an industry workshop at NIST identified the gases and properties of highest priority, and they recommended publishing the property values in a public, Web-based database. The gases include process gases, “surrogate” calibration gases, and binary mixtures of process and carrier gases. The identified properties and required uncertainties include the following.

- heat capacity at constant pressure $\pm 0.1\%$
- equation of state (gas density) $\pm 0.1\%$
- viscosity $\pm 0.5\%$
- thermal conductivity $\pm 0.5\%$

The workshop also required the following uncertainties for physical standards for gas flow.

- primary standards for gas flow $\pm 0.025\%$
- transfer standards for gas flow $\pm 0.1\%$

TECHNICAL STRATEGY

We are measuring the speed of sound $u(T, p)$ in process gases and in the surrogate gases that are often used for calibration. The speed-of-sound data have relative standard uncertainties of 0.01 %. Measurement conditions range as high as 425 K and 1500 kPa (or to 80 % of the vapor pressure for condensable gases). Figure 1 shows an example of such data. The speed-of-sound data are used to determine the ideal-gas heat-capacity $C_p^0(T)$ with the targeted uncertainty of 0.1 %. The pressure and temperature-dependences of $u(T, p)$ are correlated with model two-body and three-body intermolecular potentials. These potentials are used to calculate the virial equation of state for the density $\rho(T, p)$ and to get first estimates of the viscosity $\eta(T)$ and the thermal conductivity $\kappa(T)$. For gases where reliable data exist, we verified that results calculated in this way have uncertainties that are less than 0.1 % for density, 10 % for viscosity, and 10 % for thermal conductivity from 200 K to 1000 K.

Technical Contacts:

Robert F. Berg
John J. Hurly
Michael R. Moldover

“I was pleasantly surprised when I came across your database of thermophysical properties of gases used in the semiconductor industry. It was virtually exactly what I was searching for.”

Bob Rathfelder,
Project Engineer,
Parker Hannifin

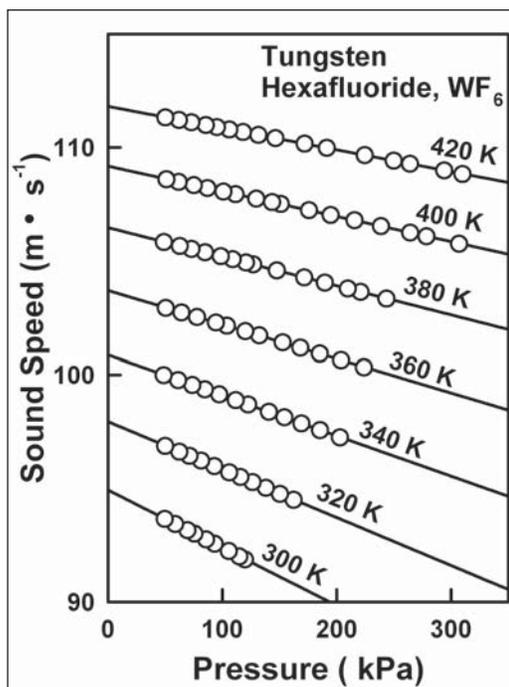


Figure 1. Speed of sound in tungsten hexafluoride as a function of pressure along isotherms.

We also are developing novel acoustic techniques to measure the viscosity and thermal conductivity with uncertainties of less than 0.5 % as specified by the industry workshop. Figure 2 shows a second-generation acoustic viscometer made from Monel. Throughout the project, the results will be made available to industry through publications in professional journals, presentations at professional meetings, and entries in an on-line database at <http://properties.nist.gov/semiprop> (see Fig. 3).

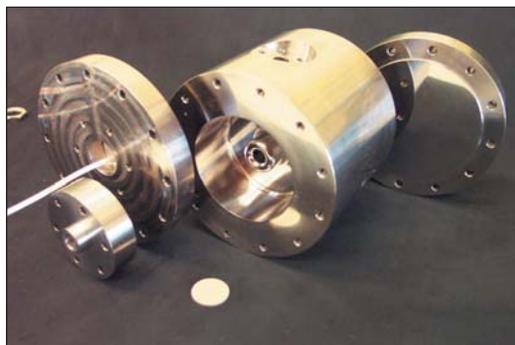


Figure 2. Second-generation acoustic viscometer made from Monel for use with corrosive gases.

Tungsten Hexafluoride		MW [1]	N.B.P. [2]	T.P. [2]
WF ₆		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

T	C _p ^o (T)	Vapor Pressure	R(T)	4R/RT	C(T)	4C/RT	λ	η
K	J/(mol·K)	MPa	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹ ·T ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹ ·T ⁻¹	mW/(m·K)	μPa·s
Estimated Uncertainty	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	-4638932	47121716	-	-
210	12.00	0.34	-1864.5	5441.0	-3653771	36754361	-	-
215	12.16	0.58	-1741.8	4994.1	-2884907	23924191	5.2	14.17
220	12.32	0.95	-1631.6	4600.8	-2291407	22349084	5.3	14.41
225	12.48	1.53	-1532.2	4252.9	-1829413	18345717	5.6	14.64
230	12.63	2.39	-1442.1	3943.9	-1466994	14767456	5.7	14.88
235	12.79	3.62	-1360.3	3668.3	-1180656	11962851	5.9	15.11
240	12.95	5.37	-1285.7	3421.6	-952936	9747555	6.0	15.30
245	13.10	7.79	-1217.5	3199.8	-770738	7985050	6.2	15.58
250	13.26	11.08	-1154.9	2999.9	-624150	6573288	6.3	15.81
255	13.42	15.47	-1097.3	2819.0	-505611	5433305	6.5	16.05
260	13.57	21.22	-1044.2	2654.0	-409306	4512569	6.6	16.28
265	13.73	28.66	-995.0	2505.4	-330731	3760214	6.8	16.51

Figure 3. Sample page from on-line database located at <http://properties.nist.gov/semiprop/>.

We have developed a diverse series of primary standards for gas flow. The first was a constant-volume (pressure rate-of-rise) primary standard that we developed to measure flows up to 10⁻³ mol/s with uncertainties of about 0.1 %. It has been replaced by a constant-pressure (variable volume) standard that can operate at pressures from 0.5–9 atmospheres. The third primary standard is gravimetric; flow measurements made by a transfer standard are integrated and compared to the weight change of a gas bottle. The second and third standards have a standard

uncertainty of 0.02 %. Figure 4 demonstrates the accuracy of the flow standards.

Transfer standards allow the primary flow standards at NIST to be compared to flow meters at other locations, such as MFC manufacturers. Although a flow meter manufacturer often uses its own primary standard, comparisons with NIST allow the manufacturer to demonstrate proficiency and, if necessary, provide traceability to NIST. For this purpose, we have developed a series of very stable transfer standards based on laminar flow through a thermostatted duct. The first generation used a stainless steel, helical duct of rectangular cross-section. It was used to perform on-site proficiency tests of industrial flow standards at fabrication facilities and MFC manufacturers. The second-generation transfer standard uses quartz capillaries with a circular cross-section, which are available commercially for gas chromatography. It has been used for comparisons with metrological institutes of other countries as well as manufacturers of flow meters. Its standard uncertainty is 0.03 %. The third-generation standard improves convenience by combining the quartz capillary with commercial instrumentation to measure pressure and temperature.

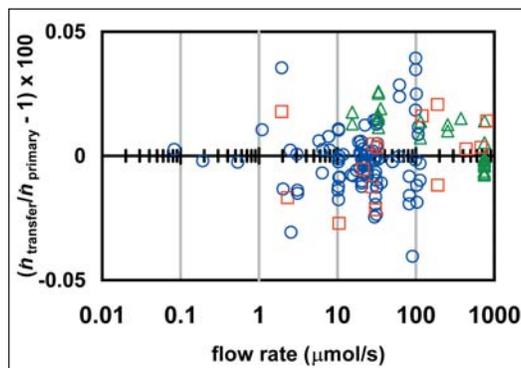


Figure 4. Comparison of three primary flow meters. The transfer standard compared the constant-pressure flow meter (circles) with the gravimetric flow meter (squares) and a constant-volume flow meter (triangles). (1 μmol/s ≈ 1.3 sccm.)

DELIVERABLES: Install new spherical resonator for measuring the speed of sound in the hazardous gases facility. 2Q 2005. Calibrate resonator by 3Q 2005.

A cylindrical resonator was used to study nine process gases, but it must be replaced due to contamination. A spherical resonator has been fabricated and will be installed in the hazardous gas handling facility. The spherical resonator will be

capable of producing higher accuracy measurements than the cylindrical resonator.

DELIVERABLES: Develop improved model of acoustic viscometer by 2Q 2005, develop model of acoustic thermal conductivity resonator by 3Q 2005.

The second-generation Greenspan viscometer incorporates lessons learned from the previous device, thereby allowing an improved acoustic model. The model of the thermal conductivity acoustic resonator will need to be tested and further developed from calibration measurements.

DELIVERABLES: Install second-generation Greenspan viscometer in hazardous gas facility by 1Q FY2005; write and test automation software by 1Q FY2005. Install gas thermal conductivity device in test facility by 2Q FY2005; write and test automation software by 3Q FY2005.

The improved Greenspan viscometer will be installed in the existing hazardous gas handling facility and the software running the apparatus modified. The thermal conductivity acoustic resonator needs to be incorporated into the facility to provide temperature and pressure control, and the computer code developed to run the system.

DELIVERABLES: From the speed-of-sound measurements, determine the ideal-gas heat capacity and equation of state for each species. Calibration gases by 2Q 2005, octafluoro-cyclobutane by 3Q 2005, and ammonia 4Q 2005.

DELIVERABLES: Measure the transport properties in the semiconductor process gases identified by the customer. Calibration gases by Q1 2005, octafluoro-cyclobutane by 3Q 2005, ammonia 4Q 2005.

Each new resonator must be calibrated with test gases such as helium and argon. After calibration and the appropriate safety assessments, the measurements of the semiconductor process gases will begin.

DELIVERABLES: Update on-line database by 4Q 2004, publish viscosity measurements in NF_3 and N_2O by 2Q 2005.

The measurements will be disseminated through papers in professional journals, talks given at professional meetings, and the on-line database.

DELIVERABLE: Submit to archival journal a paper on primary gas flow standards by 1Q 2005.

DELIVERABLE: Repackage transfer standard based on commercial measurement package by 2Q 2005.

The third-generation transfer standard will use commercial instrumentation to measure the pressures and temperature of gas flowing through a quartz capillary. The commercial instrumentation will improve the flow meter's convenience, and the quartz capillary will be the similar to that of the second-generation standard. Using the same capillary and model will ensure an uncertainty of 0.1 %. An improved design based on preliminary tests will improve the reliability of the capillary package.

DELIVERABLE: Test prototype Coriolis flow meter for gases by 2Q 2005.

Coriolis flow meters are the only devices that measure directly mass flow rate instead of a secondary quantity such as velocity or heat loss. The prototype flow meter is designed to measure the small Coriolis forces induced by flows less than 1000 sccm.

DELIVERABLE: Draft SP-250 for gas flow calibrations by 3Q 2005.

The SP-250 document will be used to establish a routine calibration service at NIST for gas flows in the range from 10^{-7} to 10^{-3} mol/s (0.1 to 1000 sccm).

ACCOMPLISHMENTS

- We designed and assembled a second-generation Greenspan viscometer. Its Monel construction allows the study of corrosive process gases.

- We measured the speed of sound in the process gases Cl_2 , NF_3 , and N_2O . Typically, the standard uncertainty of the speed of sound was less than 0.01 %. From these data the ideal-gas heat-capacity was determined to within 0.1 %, and an equation of state was developed to predict the gas densities to within 0.1 %. Viscosity was measured in these three gases plus CF_4 and C_2F_6 with an uncertainty of approximately 0.5 %.

- We continued to provide immediate access to our results by updating the database of gas properties at <http://properties.nist.gov/semiprop/>.

- We verified the accuracy of the primary flow meters by comparing the lower and upper ends of their ranges with other, overlapping NIST flow meters. Near both the lower end (0.3 sccm) and the upper end (1000 sccm) the agreement of 0.03 % was within the mutual uncertainty of the comparison.

- We used the second-generation transfer standard and a prototype of the third-generation transfer standard to make a comparison of gas flows with a manufacturer of mass flow controllers.
- We improved the temperature control of the constant-pressure primary flow meter to 0.01 K. We used additional temperature and volume measurements to further characterize this primary standard.

RECENT PUBLICATIONS

R. F. Berg and S. A. Tison, "Two primary standards for low flows of gases," *J. Res. Natl. Inst. Stan.*, **109**, 435-450 (2004).

R. F. Berg, "Simple flow meter and viscometer of high accuracy for gases," *Metrologia*, **42**, 11-23 (2005).

J. J. Hurly, "Viscosity and speed of sound of gaseous nitrous oxide and nitrogen trifluoride measured with a greenspan viscometer," *Int. J. Thermophys.*, **25**, 625-641(2004).

LOW CONCENTRATION OF HUMIDITY STANDARDS

GOALS

The primary objective is to establish quantitative standards enabling the accurate measurement of trace quantities of water vapor ($< 10^{13}$ molecules cm^{-3}). This effort supports the development and application of commercial humidity sensors used for gas purity measurements and inline monitoring and process control — functions that are relevant to minimizing wafer misprocessing.

CUSTOMER NEEDS

As discussed in the 2004 International Technology Roadmap for Semiconductors (ITRS) in the chapter entitled Metrology, the evolution of sensor-based metrology for integrated manufacturing requires the development of in-situ sensors enabling in-time measurements. In Table 115 entitled Metrology Difficult Challenges, the need for robust and accurate sensor technology and impurity detection in starting materials is highlighted. Of the known impurities in processing gases, water vapor is one of the most ubiquitous and difficult to eliminate. Thus its measurement and control is often critical to various semiconductor-related processes. The 2004 ITRS also includes greater emphasis on epitaxial processes that use gases as source materials, including SiGe and III-V semiconductor requirements in Tables 55a (for power amplifiers) and Table 121 (extension of physical models to III-V semiconductors).

Although a variety of high sensitivity sensors of water vapor are available, most do not directly measure water in the gas phase. Rather they typically respond to moisture-induced changes in bulk or surface properties associated with the adsorption of water vapor. Consequently, a rigorous first-principles determination of sensor response is often precluded, thus compromising accuracy. Moreover, since many such devices exhibit drift and poor reproducibility, frequent recalibration is required. Interpretation of these measurements is also complicated by complex physical interactions of water vapor with technical surfaces in transfer lines, in reaction chambers and in sensor housings.

TECHNICAL STRATEGY

The development of accurate and robust water vapor sensors requires well-characterized reference standards against which such devices can

be evaluated. This should include a primary method of measurement for water vapor concentration and a complementary method yielding high-precision and stable sources of water vapor. By providing access and traceability to the unique capabilities at NIST discussed below, instrument manufacturers and sensor users can assess the overall performance and accuracy of their measurements.

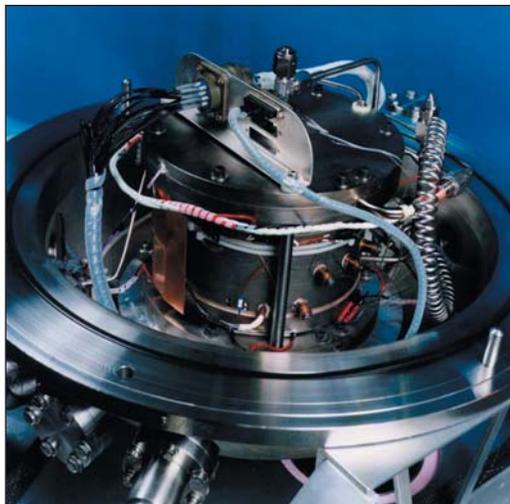


Figure 1. NIST Low Frost-Point (humidity) Generator.

Our strategy is to establish complementary capabilities in high-precision generation and measurement of water vapor. To address these respective needs, we have developed a thermodynamically based humidity source and high-sensitivity optical absorption measurement methods discussed below. The thermodynamic humidity source, known as the Low Frost-Point Generator (LFPG) (see Fig. 1 and Fig. 2), serves as the project cornerstone and is capable of delivering 3 mmol to 3 nmol of water vapor per mole of dry gas. Here the water vapor concentration in a gas stream is precisely controlled by active regulation of the saturator temperature and pressure. As such, the LFPG is ideally suited for testing the performance of various sensing and humidity generation technologies. To date, it has been used to characterize water vapor measurement and generation systems at the research and development stage as well as commercial devices.

Technical Contacts:

J. T. Hodges
D. Ripple
K. Bertness

“The LFPG is the ‘Gold’ standard for moisture generation and after the round robin experiments it is possible for the industry to talk about moisture measurements that can be compared to the standard.”

Suhas Ketkar,
Air Products and Chemicals

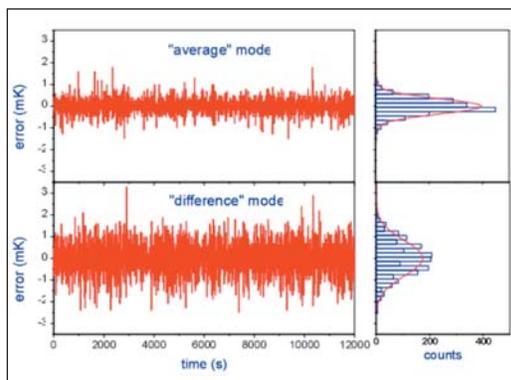


Figure 2. Steady state response of saturator control thermometers in NIST Low Frost-Point Humidity Generator.

1. A common technology used by the semiconductor industry for delivering controlled quantities of water vapor is based upon the controlled permeation of water vapor (called permeation tube generator (PTG)) through a material, followed by mixing and dilution with a dry gas of known flow rate. We have constructed a calibration system for water permeation tubes, comparing permeation tubes to the LFPG using a commercial water vapor sensor as a nulling device. This approach constitutes an efficient and low-cost mechanism for the dissemination of NIST trace humidity standards. Experience with the system has revealed several limitations of traditional implementations, including deviations of the output from the equation generally used to predict the temperature dependence of the permeation rate.

DELIVERABLES: Complete uncertainty analysis of permeation-tube calibration system. 3Q 2005. Complete study of temperature dependence of permeation tubes. 1Q 2006.

2. The basis for the LFPG as a humidity standard is knowledge of the temperature-dependent ice vapor pressure. The most commonly used correlation is that developed by Wexler of NBS. By generating a single moisture concentration either directly with the LFPG, or by diluting the water vapor/gas mixture produced by the LFPG with dry gas, we have validated the Wexler correlation.

DELIVERABLES: Quantitatively analyze and publish measurements of dilution tests. 4Q 2005

3. The LFPG is currently limited to generating greater than 3 nmol mol^{-1} of water vapor in N_2 based on the minimum achievable temperature of the saturator, and knowledge of the ice vapor

pressure discussed above. We have recently demonstrated a new strategy for pmol mol^{-1} -level humidity generation using dry-gas dilution of the water vapor/gas mixtures produced by the LFPG output streamified. Presently, we are establishing the uncertainties and optimal methodologies for this technique.

DELIVERABLES: Document methods and uncertainty of extending the LFPG to pmol mol^{-1} levels of humidity generation. 4Q 2005

4. To complement our established capability in precision generation of trace humidity levels, we are developing absolute techniques based upon the absorption of visible and near-infrared laser radiation. Water vapor has an absorption spectrum comprising thousands of distinct rovibrational absorption transitions in this spectral region. Thus, the concentration of water vapor can be readily determined in terms of measurements of sample absorbance and independently determined absorption line intensities. Recent advances in source and detector technology, and new spectroscopic techniques that extend the sensitivity of laser absorption measurements now enable the precise sensing of water vapor at concentrations below $10^{10} \text{ molecules cm}^{-3}$. To account for line broadening effects, and mitigate interference effects associated with absorption by other species the most precise absorption measurements require that individual transitions be spectrally resolved. This demands a technique having a frequency resolution much smaller than the characteristic widths of the absorption transitions, and requires that the frequency intervals in the measured spectrum be accurately determined. By combining high spectral resolution with high precision absorbance measurements, the water vapor concentration can be found independently of the composition of the carrier gas. Of the optical absorption methods, cavity ring-down spectroscopy (CRDS) is expected to be the most suitable for a primary method. CRDS is a cavity-enhanced optical absorption technique that has high sensitivity, fast response, and probes a compact well-defined volume. It is important to emphasize that under certain conditions, CRDS can exhibit exceptional spectral resolution, enabling detailed measurements of absorption line shape. To this end, we have developed a refined version of CRDS called frequency-stabilized single-mode cavity ring-down spectroscopy (FSSM-CRDS). Here, the ring-down cavity is actively length stabilized, the probe laser is frequency locked to the ring-down cavity, and the

frequency axis of the spectra is based upon the longitudinal mode spacing of the ring-down cavity (see Fig. 3).

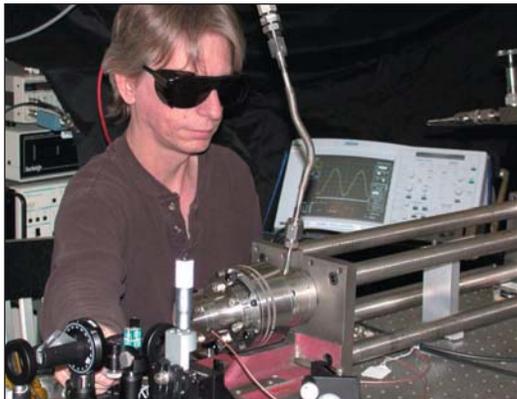


Figure 3. Frequency-stabilized CRDS system.

Using the existing FSSM-CRDS apparatus, appropriate transfer standard generators and hygrometers, we will link H₂O transition line intensities to thermodynamic-based LFPG. Taking advantage of the high spectral resolution afforded by FSSM-CRDS, various line shape effects such as speed-dependent pressure-broadening and collisional narrowing of these transition line shapes by various media will also be quantified.

DELIVERABLES: Link H₂O transition line intensities to LFPG for water vapor concentration measurements in the range 10 nmol mol⁻¹ to 100 μmol mol⁻¹ and measure line shape effects in N₂ and other gases. 3Q 2005.

5. Moisture contamination is a serious problem in phosphine, arsine, silane, ammonia, and similar gases used in the epitaxial growth of high-purity semiconductor layers. Semiconductor device manufacturers have expressed frustration with the irreproducibility of source material purity from vendor lot to vendor lot. The critical concentrations of the impurities are not well known; however, it is believed that >10 nmol/mol oxygen or water in most process gases is undesirable. Optical methods for measuring the moisture impurity concentrations combine high sensitivity and straight-forward traceability through the LFPG absorption line strength measurements. In collaboration with researchers in the NIST Chemical Science and Technology Laboratory, researchers in the NIST Electronics and Electrical Engineering Laboratory have developed a CRDS system linked with a semiconductor crystal growth system to measure H₂O at very low concentrations in semiconductor source gases and to correlate

the process gas impurities with crystal properties. The system is being used to measure the lineshape, absorption coefficients, and frequency of optical transitions for water, phosphine, and ammonia in the vicinity of 935 nm and 1380 nm. This information is critical to facilitate the use of high-sensitivity spectroscopy techniques in these gases. The laboratory is equipped to allow safe handling of toxic gases such as phosphine and arsine, enabling collaborative experiments with industry on direct measurements of moisture in those gases. The CRDS capability should ultimately lead to improvements in semiconductor source gas purity, which will allow crystal growers to choose less expensive growth conditions without sacrificing optical emission efficiency and yield in LEDs, semiconductor lasers, and photodetectors.

DELIVERABLES: Modify CRDS system for parallel tests with commercial instrumentation and conduct joint experiments on H₂O in phosphine. 3Q 2005

Measure phosphine absorption lines in vicinity of H₂O transition line at 943.082 nm and compare to previous H₂O lines explored for overlap with phosphine. If new line offers superior sensitivity, measure pressure broadening coefficients for H₂O in phosphine. 4Q 2005

ACCOMPLISHMENTS

■ We have constructed a permeation tube calibration facility (see Fig. 4). The purpose of this system is to provide measurement traceability for industrial users of permeation tube humidity generators. The calibration system comprises a custom PTG, the LFPG and high-sensitivity quartz crystal microbalance (QCM). The water-containing permeation tubes to be calibrated are placed inside the temperature-stabilized PTG oven. Water vapor diffuses from the tube surface into a precisely controlled stream of purified N₂. The diluent gas flow rate is adjusted so that the



Figure 4. New PTG calibration apparatus.

water vapor concentration produced by the PTG is equivalent to that produced by the LFPG, as measured by the QCM. From these measurements the water permeation rate of the tube under test can be determined in terms of the known LFPG output. As seen in Fig. 5, the calibrations derived from this system are repeatable to approximately 1 %, which is significantly superior to traditional gravimetric methods.

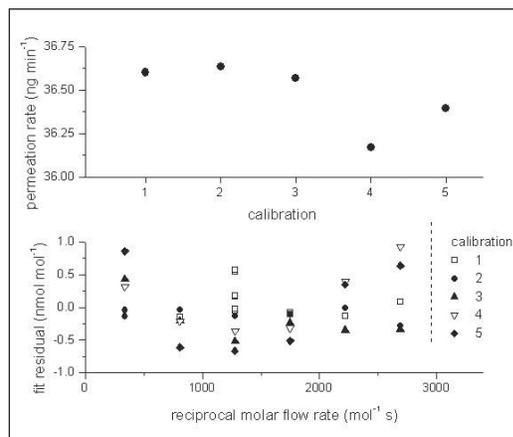


Figure 5. Calibration repeatability (top) and deviations from the fitting function (bottom) of a water-vapor permeation tube in the NIST Permeation Tube Calibration Facility.

■ A new strategy for pmol mol^{-1} (ppt) -level humidity generation has been successfully implemented. The approach, shown in Fig. 6, involves the controlled dilution of water vapor/gas mixtures produced by the LFPG, using a flow dilution system similar to that incorporated within the PTG calibration system described above. A check of the consistency of the ice vapor pressure correlation used at NIST was performed over the temperature range between $-95\text{ }^{\circ}\text{C}$ to $-82\text{ }^{\circ}\text{C}$. A nominally constant humidity test point of 14 parts per billion (ppb) was produced by diluting water

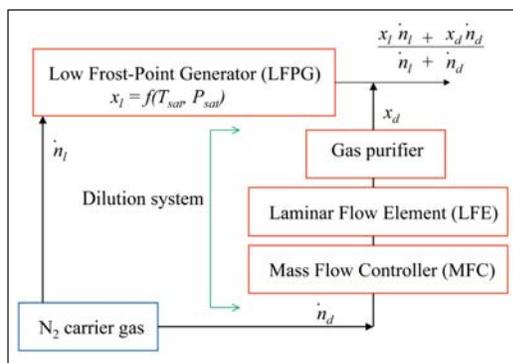


Figure 6. Proposed dilution system for extending the LFPG operating range to pmol mol^{-1} levels.

vapor / nitrogen mixtures from 14 ppb to 140 ppb with purified nitrogen. Measurements obtained using a quartz crystal micro-balance produced the same humidity value for all points, within the expected uncertainty of the system of analyzer and connecting tubing.

■ The LFPG uncertainty analysis is based on the uncertainties in temperature and pressure within the LFPG saturator, ice vapor pressure and the enhancement factor for mixtures of water vapor and air. However, this analysis neglects background effects associated with the transient adsorption and desorption of water vapor from internal surfaces in the flow manifold located downstream of the LFPG. For the lowest range considered, such processes may affect significantly the water vapor concentration in the sample gas delivered by the LFPG to test instrumentation. In collaboration with Air Products Inc., we quantified the magnitude of this water vapor background using atmospheric pressure ionization mass spectrometry (APIMS). Results, shown in Fig. 7, indicate that the background contribution to H_2O from system components downstream of the LFPG was less than 0.2 nmol/mol . These measurements also demonstrated that linearity deviations of the LFPG output H_2O mole fraction are less than 0.1 nmol/mol .

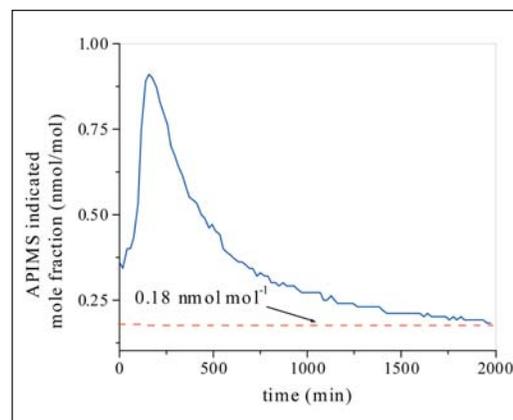


Figure 7. APIMS measurement of LFPG background H_2O concentration showing decay to steady state level.

■ We have successfully developed an FSSM-CRDS system to study the optical absorption of trace levels of water vapor with a resolution and accuracy unobtainable with other techniques. The system is based on a near-infrared continuous wave diode laser emitting over the range 917 nm to 943 nm. The gas sampling system is optimized for high-precision measurements of trace water vapor

concentration. The flow system has all-metal seals, low dead volume, and active mass flow rate and pressure regulation. Background levels $< 0.5 \text{ nmol mol}^{-1}$ (background equivalent) have been demonstrated. The FSSM-CRDS method was used to probe water vapor absorption transitions in the 936-nm spectral region. In conjunction with humidity standards for determination of water vapor concentration, these spectroscopic measurements yielded relative uncertainties in line intensities less than 1%. Figure 8 shows measured spectra (symbols) and theoretical spectra (solid lines) for a pair of overlapping water vapor absorption transitions, each case corresponding to a given total gas pressure (with N_2 as the buffer gas). These results illustrate that the spectral resolution and linearity of the FSSM-CRDS method enable precise quantification of pressure broadening, collisional narrowing and asymmetries of the absorption line shape, thus minimizing systematic errors in the determination of number density and line intensity that typically arise from instrumental line broadening effects. Also, detection limits less than 10 nmol mol^{-1} of H_2O in N_2 have been demonstrated, using the relatively weak absorption lines near 935 nm accessible with the near-ir diode laser used in this system.

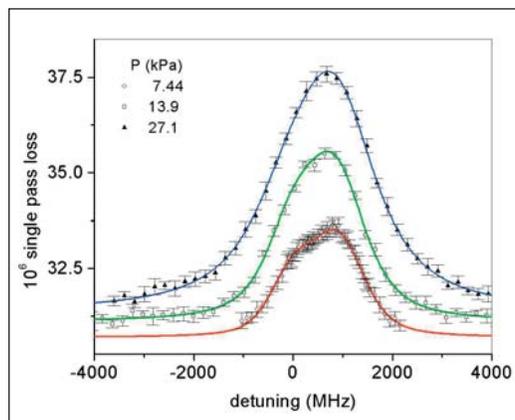


Figure 8. High-resolution FSSM-CRDS spectrum of a pair of pressure-broadened water vapor absorption transitions. Symbols are experimental points, and lines are Voigt fits to the measured profiles.

We have used a similar FSSM CRDS system to measure water vapor concentrations in the toxic gas phosphine in the 935-nm spectral region. Testing of five strong water absorption lines in this region indicated that the least overlap with phosphine lines, and hence the highest sensitivity to water contamination, is present for the line at 943.082 nm. Future experiments will characterize

this line for pressure broadening coefficients and ultimate sensitivity limits. Figure 9 shows a typical H_2O spectrum obtained with the automated FSSM-CRDS system and comparison with previously published measurements.

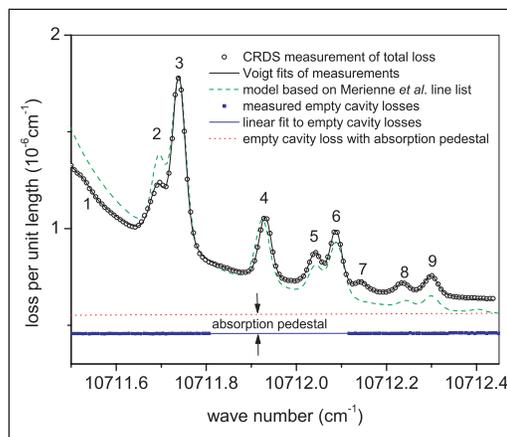


Figure 9. Survey spectrum of water vapor obtained with frequency stabilized CRDS apparatus. The numbers correspond to peaks of individual absorption transitions.

COLLABORATIONS

Air Products and Chemicals Inc., Seksan Dheandhanoo; APIMS measurements of trace moisture and characterization of semiconductor gas purity.

Matheson Tri-Gas, Mark Raynor and Hans Funke; CRDS measurements of trace moisture in phosphine.

Tiger Optics, Yu Chen; CRDS measurements of trace moisture in phosphine.

Dow Chemical, Linh Le and J. D. Tate; CRDS measurements for process gas control RH Systems, Robert Hardy; Characterization of low range chilled-mirror hygrometers and humidity generators for standards laboratories.

Southwest Sciences Inc, Chris Hovde.; Development of wavelength modulation laser hygrometer for trace H_2O sensing.

Tiger Optics, Calvin Krusen ; evaluation of commercial CRDS technology.

Air Products and Chemicals Inc.; CRDS measurements of trace H_2O in corrosive process gases.

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D. C. Hovde, J. T. Hodges, G. E. Scace, J. A. Silver, "Wavelength-modulation laser hygrometer for ultrasensitive detection of water vapor in semiconductor gases," *Appl. Opt.*, **40**, 829-839 (2001).

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TEMPERATURE MEASUREMENTS AND STANDARDS FOR RAPID SEMICONDUCTOR PROCESSING

GOALS

The goal is to develop the technologies required to enable the improved accuracy of temperature measurements in semiconductor wafer processing as prescribed in the International Technology Roadmap for Semiconductor (ITRS).

Our project, initiated in 1997, has resulted in improved calibration wafer technology based on thin-film thermocouples (TFTCs) in conjunction with wire thermocouples (TCs) on test wafers for in-tool radiation thermometer (RT) calibration, achieving a 2 °C standard uncertainty of measurements in rapid thermal processing (RTP) tools. We have also developed improved procedures for the calibration of lightpipe radiation thermometers and theoretical models for the relationship between the true wafer temperature and the indicated radiance temperature. With the completion of this work, we are now focusing on: 1) collaborating with the semiconductor industry in implementing new methods for reliable and traceable temperature measurements, 2) developing new resistance sensors for the range 300 to 600 °C, and 3) understanding measurement errors when calibration wafers are used in non-isothermal environments.

CUSTOMER NEEDS

The measurement needs of the semiconductor manufacturing industry have been stated in the ITRS. The requirement is for measurement and control of RTP tools to ± 2 °C during dopant anneal with calibrations traceable to the International Temperature Scale of 1990 (ITS-90). In the 2004 edition of the ITRS in the section on "Metrology Difficult Challenges" the roadmap states "Better sensors must be developed for ... wafer temperature measurement during RTA."

Current needs include better temperature measurement uncertainty in post exposure bake (PEB) processing of resists and in rapid thermal processing (RTP) of wafers including silicide formation in the temperature range of 300 °C to 700 °C. Understanding differences of temperature readings between different instrumented wafers is also a high priority.

Our customers are the device manufacturers and the suppliers of thermal processing equipment and temperature measurement instrumentation.

This community forms our project's Common Interest Group (CIG), 20 companies meeting annually since 1997. They serve as a bridge between research and practice, provide advice on shaping objectives, and generate opportunities for technology transfer. We have had our NIST patented thin-film thermocouple wafer evaluated at the ISMT (Sematech)/ University of Texas RTP LPRT test facility and at Vortek Ltd. manufacturers of RTP tools. Currently Applied Materials and Atmel, both RTP tool manufacturers, are evaluating the NIST test wafer.

TECHNICAL STRATEGY

Our research is focused on four projects that will enable the semiconductor industry to meet the roadmap requirements: (a) support our industrial collaborators in the use of test wafers with improved thin-film technology to demonstrate in-tool calibration of RTs traceable to the ITS-90, (b) develop new, accurate sensors for the 300 °C to 700 °C range, where commercial sensors are inadequate, (c) investigate effects on measurements of imperfect thermal environments, and (d) develop silicon-wafer emittance standards for improved temperature and emittance measurements.

Cooperative projects with Applied Materials and Atmel industries are investigating the use of the NIST calibration wafers in industrial RTP tools. These evaluations are critical for transferring the NIST developments to the semiconductor processing industry. The NIST TFTC calibration wafer has demonstrated unique capabilities in temperature measurements and in establishing traceability to the ITS-90. We have also prepared a document "Instructions for use of the NIST Thin-Film Thermocouple Calibration Wafer" in response to requests from our CIG. It is being reviewed by our users and will be finalized by 12/31/05.

DELIVERABLES: NIST TFTC calibration wafers and instructions for application of NIST calibration wafer, and joint report with Applied Materials and Atmel on LPRT calibrations. 3Q 2005

Members of our CIG have also asked us to develop calibrated thin-film resistors for wafer temperature measurement from 300 °C to 600 °C. These measurements are needed for more accurate control of the silicide anneal RTP. We have

Technical Contacts:

D. Ripple
B. Tsai

"On behalf of SensArray Corporation, I express our deep gratitude to NIST for significantly contributing to advances in semiconductor lithography process optimization and control. NIST has contributed to improved CD control in lithography processes through the establishment of measurement methods and standards for wafer thermal bake cycle dynamics in resist processing. This support is just in time, as the next area of focus for photo resist processing optimization is bake cycle dynamics. Your work will be of value to every advanced semiconductor factory."

*Wayne Renken, President
SensArray Corp.*

undertaken the development of precision platinum thin-film RTDs directly on the silicon wafers to improve the uncertainty of *in situ* wafer temperature measurement at these temperatures. Initial results are promising, and have motivated new work concentrating on reducing hysteresis and uncertainty, and on achieving high and repeatable values of the thermal coefficient of resistivity.

DELIVERABLES: Report on the uncertainty and temperature range of thin-film Pt resistor thermometers directly on Si wafers. 3Q 2006

As a first step in determining the sensitivity of a sensor on an instrumented wafer to a non-isothermal environment, it is necessary to measure the thermal resistance between the sensor and the silicon substrate. We are developing a technique where the temperature of the silicon wafer is modulated, and the response of the sensor measured synchronously. Simple theoretical models can be fit to the data to ascertain the thermal resistance between sensor and wafer. This technique is envisioned as a useful quality-assurance tool for manufacturers of instrumented wafers.

DELIVERABLES: Paper on measuring the thermal response time of commercial embedded sensors. 3Q 2005.

CIG meetings have been held annually since 1997 for the purposes of assessing and planning project research directions, and for fostering collaborative work with equipment suppliers, chip makers, and instrumentation suppliers. At the 12th International Conference on Advanced Thermal Processing of Semiconductors (RTP'04, Sept., 2004, Portland, OR), the meeting addressed several major needs in temperature measurement. We had requests by our industrial collaborators for test wafer demonstrations and discussions on proposals for establishing emittance standard wafers. At RTP'04 our team organized two regular conference sessions under the theme of traceability of RTP temperature measurements. Papers were presented on TC and RT calibrations methods and thermal modeling. A panel discussed plans for an industry-wide emittance standards initiative. An important contribution by NIST to the initiative is the use of the high temperature properties measurement facilities to generate a reliable, traceable database and to validate optical properties models.

DELIVERABLES: Organize and conduct CIG meeting on traceable temperature measurements at key industry RTP conference. 4Q 2005

ACCOMPLISHMENTS

DEVELOPMENT OF RESISTANCE SENSORS FOR 300 °C TO 700 °C APPLICATIONS

We have explored the performance of platinum resistance thermometers deposited directly on oxide-coated silicon wafers. Our work has measured the effects of thickness and bond coat (Ti or Zr) of the Pt thin films. We have also measured the effect of ambient atmosphere (air or nitrogen) on the hysteresis and thermal coefficient of resistivity, α . The value of α was not sensitive to the annealing temperature or Ti bond-coat thickness, but did depend on the Pt thickness.

CALIBRATION OF LPRTS IN THE RANGE 300 °C TO 700 °C

LPRTs have become mainstream in the temperature measurement in the RTP community. We have calibrated LPRTs for RTP applications using a sodium heat-pipe blackbody between 700 °C and 900 °C with an uncertainty of about 0.3 °C ($k=1$) traceable to the ITS-90. Recently, cable-less LPRTs (CLRTs) offer a decisive advantage to enable radiometric measurements at lower temperatures than traditional LPRTs. New application of CLRTs can eliminate 2.0 °C or more uncertainty from the calibration scheme. We have used the NIST RTP Test Bed to perform intercomparisons between the TFTCs and the new low-temperature (300 °C to 700 °C) CLRTs. Our study has established calibration uncertainties for comparison of CLRTs against the TFTCs *in situ*, and has established uncertainties for model-corrected CLRTs calibrated against blackbodies.

LIGHTPIPE PROXIMITY

We designed an experimental and analytical study to quantify the lightpipe proximity effect and provide a model for industrial users of LPRTs to correct their LPRT readings. The experiments employed TFTC wafers, our RTP test bed, and LPRT readings to characterize the effects of lightpipe proximity on wafer temperatures. We found that the wafer temperature can be depressed more than 20 °C by positioning the lightpipe tip too close to the wafer. These results were presented in a paper for the 2003 International Conference on Characterization and Metrology for ULSI Technology and at the 2003 10th International Conference on Advanced Thermal Processing of Semiconductors (RTP 03).

TRANSIENT RESPONSE OF TEMPERATURE SENSORS DURING THE POST EXPOSURE BAKE PROCESS

Recent studies on dynamic temperature profiling and lithographic performance modeling of the PEB process have demonstrated that the rate of heating and cooling may have an important influence on resist lithographic response. We conducted an experimental and analytical study to compare the transient response of commercial, embedded platinum resistance thermometer (PRT) sensors with surface-deposited TFTCs. A dual instrumented wafer for PEB evaluation is shown in Fig 1. Experiments were performed on a commercial module using wafers instrumented with calibrated type-E TFTCs and commercial PRTs.

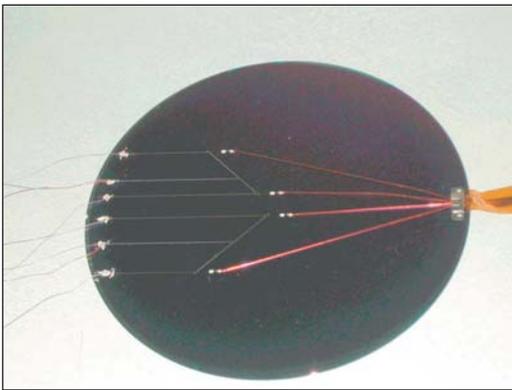


Figure 1. Wafer instrumented with PRTs and type-E thin-film thermocouples.

We measured the temperature of 200 mm Si wafers in a commercial-type PEB module using both embedded PRTs and thin-film thermocouples (TFTCs) through a typical thermal cycle from ambient, to 150 °C, and back to ambient. The transient response of the TFTCs led the PRT sensors, indicating a PRT lag (typically) of 2 °C on heating and up to 4 °C on cooling for several seconds. The wafer time constants for response were strongly affected by the air gap distance between the wafer and hot plate as expected. Thermal models were presented that showed estimates for heating time constants in good agreement with experimental data. Lithography simulation results were presented that showed the effects of transient and offset temperature profiles on CD variations.

CALIBRATION OF PRT SENSORS FOR INSTRUMENTED WAFERS

Calibration of PRTs that have been imbedded in instrumented wafers presents a challenge for the manufacturer: the wafers are much larger than commonly calibrated thermometers, the calibration process cannot contaminate wafers intended for use in a semiconductor-processing facility, and the uncertainty requirements for PEB applications are fairly demanding (standard uncertainty of approximately 0.01 °C). To validate the methods used in industry, a commercial instrumented wafer was calibrated both by NIST and by the manufacturer in the range 15 °C to 95 °C. The results were well within the stated manufacturing tolerance of the wafer and our expectations for the sensors used on the wafers.

EMITTANCE STANDARDS INITIATIVE

During the RTP 2003 Meeting in Charleston, SC, a whole session was dedicated to the introduction of the emittance standards initiative. The session was opened by comments from Steve Knight, the NIST OMP Director, who explained the role of NIST in the initiative. Three talks focused on NIST's role in the initiative and explained the NIST room-temperature reflectance facility, the NIST high-temperature emittance facility, and experimentally validated optical property models for semiconductor materials. The climax of the meeting occurred when a panel of experts in the RTP industry discussed the need for creating emittance standards with measurements traceable to NIST and explained what the standards would entail. A summary of conclusions and action items were listed, and the final outcome was the unanimous desire and support for creating emittance standards, as voiced by the panel. Invitations were issued to five different RTP manufacturers and users, who had expressed a need for emittance standards. To date, four of the five vendors have already submitted sets of silicon wafer standards for measurement. The high-temperature facility is being set up to commence characterization of the standards.

LASER-REFLECTOMETER RADIATION THERMOMETER

A Laser-Reflectometer Radiation Thermometer (LRRT) employs a reflectometer to measure normal reflectance and Kirchoff's Law to calculate the emissivity. The measurements of the emissivity and the radiance temperature can be

combined to determine the true surface temperature. Although alignment was very sensitive and frequent *in-situ* emissivity calibrations with the LRRT was necessary, the measured emissivity values differed from NIST measurements with the Spectral Tri-function Automated Reference Reflectometer (STARR) facility by less than 2 %, while the measured temperatures differed with the NIST thin-film thermocouples by less than 4 °C. With improvements in the LRRT, it is possible to take advantage of the emissivity measurement to make a more accurate temperature measurement of the wafer during processing.

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PLASMA PROCESS METROLOGY

GOALS

To provide advanced measurement techniques, data, and models needed to characterize plasma etching and deposition processes important to the semiconductor industry, enabling continued progress in model-based reactor design, process development, and process control.

CUSTOMER NEEDS

To fabricate future generations of devices, the semiconductor industry requires improvements in plasma etching and deposition processes. Plasma processes and equipment face increasingly stringent requirements due to the need to maintain high device yields at decreasing feature sizes, the introduction of new dielectric materials, and the constant pressure to keep production efficiency high. To meet these challenges, the 2004 update to the International Technology Roadmap for Semiconductors (ITRS) identifies a need for better, more predictive modeling of the impact of equipment on process results (Modeling and Simulation section, page 11, Table 122c). To obtain more reliable predictions of the chemical, physical, and electrical properties of processing plasmas, the dependence of these properties on processing equipment, and the effect of these properties on process results, further progress in model development and validation is required. The ITRS also identifies a need for development of robust sensors and process controllers (Metrology section, page 2, Table 115) which are able to convert large quantities of raw data into information useful for improving manufacturability and yield.

TECHNICAL STRATEGY

Our multifaceted program provides numerous outputs to assist our customers, including advanced measurement methods, high-quality experimental and fundamental data, and reliable, well-tested models of plasma behavior.

First, we develop and evaluate a variety of *measurement techniques* that provide industry and academia with methods to characterize the chemical, physical, and electrical properties of plasmas. The techniques we develop include improved laboratory diagnostic measurements for use in research and development, as well as more robust, non-perturbing measurements for use in process monitoring and control in manufacturing applications.

In addition to measurement techniques, we also provide *data* necessary for gaining an understanding of complex plasma properties and for testing and validating plasma models. The data help semiconductor manufacturers and plasma equipment manufacturers to better understand and control existing processes and tools and help them to develop new ones. The experimental data we provide are measured under well-defined conditions in highly-characterized standard plasma reactors. Our reactors include capacitively coupled cells as well as inductively coupled, high-density plasma reactors, one of which is shown in Fig. 1.

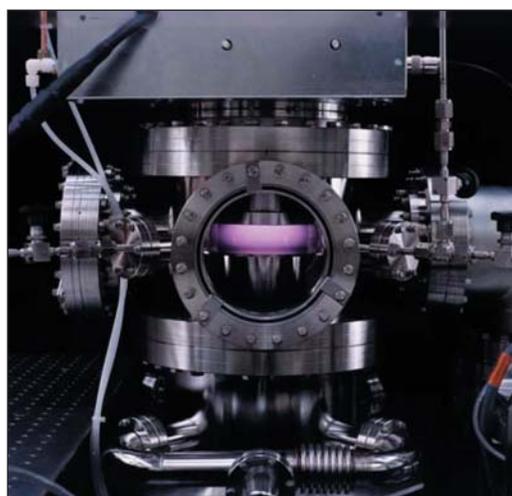


Figure 1. One of the inductive, high-density plasma reactors used in our experimental studies.

Finally, we are engaged in the development and validation of plasma *models*. Such efforts concentrate on modeling of plasma sheaths, the thin regions at the boundary of the plasma. Sheaths play a dominant role in determining discharge electrical properties and the properties of the highly energetic ions that are necessary for plasma etching. More accurate sheath models are needed to better predict and optimize discharge electrical characteristics and ion kinetic energies. Sheath models are also used to develop new types of process monitoring techniques based on radio-frequency electrical measurements.

Our ongoing and planned efforts focus on measurement, data, and modeling challenges in the following specific areas:

1. An electrical measurement technique developed at NIST for use in process monitoring and

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M. Sobolewski
K. Steffens
E. Benck

“NIST is one of the leaders in plasma processing related research in the U.S. They have capability to thoroughly understand plasma behavior using a variety of diagnostics tools.”

Peter Ventzek
Motorola

“The NIST plasma process metrology group has helped us to understand the fundamental physical and chemical processes that are important to electronics materials and semiconductor processing industries.”

Bing Ji,
Air Products and
Chemicals, Inc.

control applications continues to be the subject of further testing and validation. This technique relies on noninvasive, nonperturbing measurements of the radio-frequency (rf) current and voltage applied to plasma reactors. The rf measurements are compatible with commercial reactors and they contain valuable information about the flux and energy of the ions that bombard wafers during processing. Values for the total ion flux and ion energies are obtained by analyzing the current and voltage signals using electrical models of the plasma and its sheaths. To validate the technique, experiments in an rf-biased, inductively coupled plasma reactor have been performed both with and without silicon wafers loaded in the reactor. Plasma potentials, sheath voltages, total ion currents, and ion energy distributions obtained from the rf measurements have been compared against independent measurements and shown to be in good agreement. The technique has been used to monitor long-term drift in ion energy and total ion flux. We have also monitored the more rapid changes that occur when the pressure, power, and gas flow are perturbed in ways that mimic equipment faults. Future efforts are directed towards demonstration of the usefulness of the technique in industrial plasma reactors. We have begun a collaboration with an industrial company in which we will perform tests in a prototype commercial reactor equipped with an electrostatic chuck. The tests will evaluate the validity and usefulness of the NIST-developed electrical measurements, models, and analysis techniques in the commercial reactor.

DELIVERABLES: Evaluate the validity and utility of rf measurement techniques, electrical models, and analysis techniques in a commercial plasma reactor. 2Q 2006

2. A new method for measuring electron number density in plasmas, the wave cut-off method, has recently been developed at KRISS, the Korea Research Institute of Standards and Science. The technique can be used to characterize spatial variations in the electron density without many of the disadvantages of traditional Langmuir probe measurements. Information provided by the wave cut-off technique, if it is shown to be of sufficient reliability and accuracy, would be of use in the further development and testing of plasma models. It would also provide a better understanding of important electron collisions in plasmas as well as the factors that influence plasma spatial uniformity. We will be collaborating

with a guest researcher from KRISS to implement the wave cut-off technique in our laboratory and to evaluate its accuracy and usefulness.

DELIVERABLES: Implement and evaluate the wave cut-off method for measuring electron density in plasmas. 2Q 2006

3. Many industrial plasma etchers are equipped with optical emission spectrometers, which have proven useful for endpoint detection, fault detection and classification, and automatic process control. At present we are planning and initiating experiments in which optical emission measurements will be combined with the noninvasive electrical measurements described in item 1, above. Optical emission complements the electrical measurements by providing information about drift or other changes in the chemical species within the plasma—information that would be difficult or impossible to obtain solely from electrical measurements. We will evaluate whether data provided by optical emission can be used by the electrical analysis algorithms to obtain increased accuracy in ion current and ion energy monitoring. We also plan to assess the relative merits of optical and electrical detection of various types of process drift, equipment faults, and other changes such as etch endpoint.

DELIVERABLES: Compare sensitivity and utility of optical emission and electrical techniques for monitoring drift in etching reactors. Evaluate improvements gained by combining electrical and optical emission measurements. 4Q 2005

4. Dual frequency capacitively-coupled plasma (CCP) sources are becoming increasingly important in semiconductor manufacturing processes, however, there appear to exist only limited amounts of published data on these plasma sources. Most experimental papers concentrate solely on the source etching characteristics, and numerous theory papers on the dual-frequency sources show few comparisons with actual experimental data. We will address several issues related to dual frequency sources, concentrating on how the sheath is affected by the dual frequencies. How does applying the two rf frequencies to a single electrode compare with applying the frequencies to separate electrodes? How does varying the two frequencies modify the plasma? How independent is the ion energy control and plasma production? We will obtain time-resolved (0.5 ns) spectrographic data from the entire plasma. This data will be combined with measurements of the voltage and current

waveforms. In addition, plasma density will be measured by either microwave interferometry or a plasma frequency cut-off technique.

DELIVERABLES: Measure time-resolved (0.5 ns) spatially-resolved optical emission and plasma electrical characteristics in dual frequency plasmas to determine the effect of dual frequency on plasma characteristics. 2Q 2006

ACCOMPLISHMENTS

■ The NIST-developed, noninvasive, model-based electrical technique for monitoring ion energy and total ion flux has recently been validated in actual etching conditions in CF_4/Ar plasmas (Fig. 2). Unlike previous validations, performed with no wafer present, the recent validations were performed with silicon wafers — oxidized and bare — loaded into the reactor. The wafer, as well as the contact between the wafer and the electrode on which it rests, both contribute an electrical impedance which, if unaccounted for in the model, can cause errors in the ion energy distributions and total ion flux obtained from the noninvasive technique. At low rf bias frequencies < 100 kHz, the contributed impedance was large, resulting in substantial errors in the noninvasive results. Nevertheless, at bias frequencies of 1 MHz or higher, which are more typical of semiconductor manufacturing, the wafer and wafer contact contribute only a few ohms of impedance, resulting in an uncertainty in noninvasive ion energies of only a few electron volts. The speed of the analysis algorithms has also recently been greatly increased, making it possible to monitor changes in ion energy and total ion flux with a time resolution on the order of 1 second. In recent demonstrations,

the speeded-up technique has been used to monitor small changes in ion energy and total ion flux that occur over the course of a “normal” oxide etch, as well as larger changes that occur when the pressure, power, and gas flow were perturbed in ways that simulate equipment faults.

■ Sub-millimeter wave absorption spectroscopy is being developed as a plasma diagnostic to identify and monitor species in etching plasmas (Fig. 3). Sub-mm wave spectroscopy can monitor the crucial chemical species in a plasma and provide the necessary feedback for understanding plasma processing. This technique was used to measure radical densities in several fluorocarbon: oxygen: argon etching plasmas. The etching rate of SiO_2 in these types of plasmas exhibit a local maxima as a function of the oxygen to fluorocarbon ratio. The sub-mm absorption measurements in C_4F_6 and C_4F_8 containing discharges showed increasing CF and CF_2 radical densities with decreasing oxygen to fluorocarbon ratios for ratios below the SiO_2 etching maximum. In addition, absorption measurements of CO and COF_2 indicate that surface etching of the wafer plays an important role in the CO, but not the COF_2 , radical production. The influence of wafer coatings on the plasma was investigated by comparing the radical densities with different photoresist coated wafers (two types of 157 nm photoresist and an I line photoresist) in an etching plasma. No significant difference was observed between the CF densities for the different wafer coatings, but there was a significantly higher CF_2 density with the I line photoresist than the 157 nm photoresists tested. Time-resolved density measurements demonstrated that plasma conditions were changing during the etching of a single wafer. Both CF

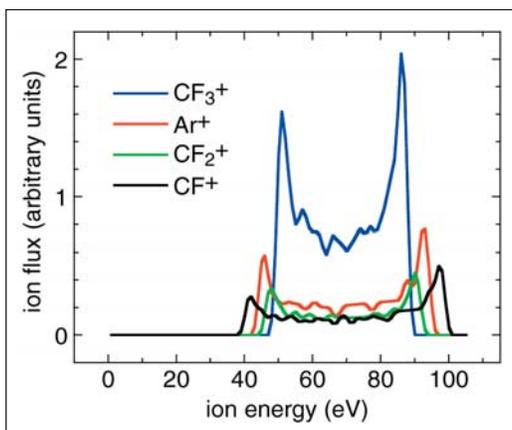


Figure 2. Ion energy distributions from noninvasive electrical measurements, determined in real-time during an oxide etch in an Ar/CF_4 plasma.

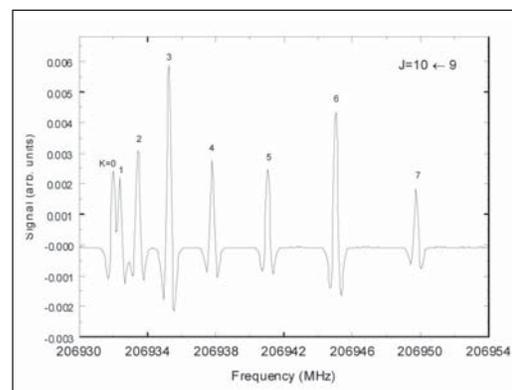


Figure 3. Sub-millimeter wave absorption spectrum of CHF_3 in a high-density, inductively coupled plasma.

and CF_2 demonstrated a gradual rise for the first ~100 seconds followed by relatively constant levels which is probably due to the development of fluorocarbon layers within the plasma etching chamber. The density of CHF_3 showed a strong spike at the start of the discharge which rapidly decayed to a low level during the remainder of the wafer etch, even though no hydrogen containing feed gases were being used. The hydrogen is probably originating from the dissociation of residual water vapor in the vacuum chamber. Together these measurements illustrate the usefulness of sub-mm spectroscopy for providing a useful understanding of plasma radicals and its potential as a process monitoring tool.

■ We have also developed the capability to measure spatially resolved 2-D temperature maps in fluorocarbon plasmas using planar laser-induced fluorescence (PLIF) of the CF radical (Fig. 4). Several PLIF images are measured, each probing a different rotational level to give a 2-D map that is related to the CF population in the probed rotational state. With the relative population for several rotational levels known at each location, a rotational temperature map is calculated and assumed to be equivalent to the gas temperature under these conditions. We have measured temperature maps in CF_4 plasmas as a function of pressure and power, with and without silicon wafers present. Simultaneously, CF density images were obtained. Under our conditions, radial variations in temperature from 10 K to 90 K were observed. Axial temperature gradients were also observed to be quite large, especially under our highest pressure conditions (800 mTorr or 107 Pa). The strongest temperature gradients were consistently found near the cooled electrode surfaces. These variations can have strong implications. Species density measurements that probe a specific rotational level can be misleading if the population of the chosen rotational level is not constant within the temperature range investigated. In addition, gas density in hotter regions will be lower, and this must not be interpreted as a chemical effect. Especially near surfaces, where species density fluxes are often interpreted as indicating surface chemistry, one must be aware of the implications of these temperature effects. In addition, understanding temperature is important for modeling, since chemical reaction rates are often a function of temperature.

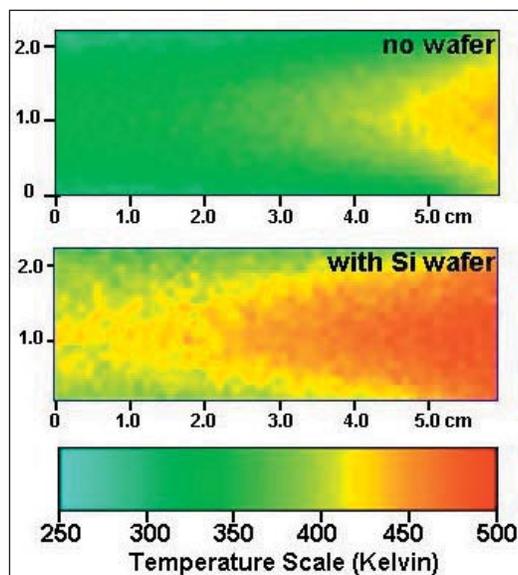


Figure 4. Temperature maps of a capacitively coupled CF_4 plasma at 200 mTorr, with and without a silicon wafer.

■ Fundamental data continue to be distributed to plasma modelers throughout industry and academia via the Web-based NIST “Electron Interactions with Plasma Processing Gases” database (<http://eeel.nist.gov/811/refdata/>) (Fig. 5). This Web site has experienced tens of thousands of hits throughout its history.

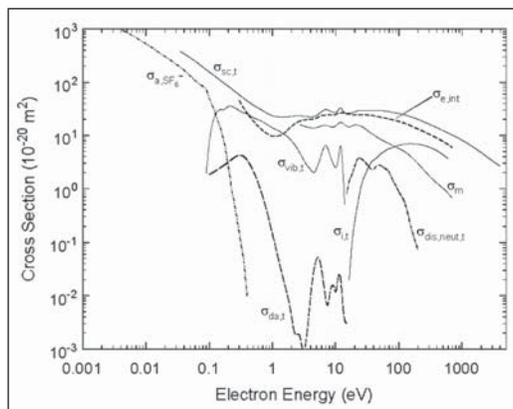


Figure 5. Recommended electron cross section data for SF_6 (shown here) and many other plasma processing gases are available at <http://eeel.nist.gov/811/refdata/>.

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