**Results of the workshop on physical properties of gases and liquid precursors**

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25 July 2006

This two-hour SEMI workshop was held on 12 July 2006 in conjunction with Semicon West in San Francisco. Its goal was to suggest directions for research on the physical properties of gases and liquid precursors. After hearing brief introductions by the organizers, the 25 participants discussed the following four topics.

1. *Which gases should be measured next?*
2. *Which liquid precursors should be measured?*
3. *What properties of liquid precursors are most important?*
4. *Are the data efficiently available?*

## 1. Which gases should be measured next?

Appendix A lists the semiconductor gases whose properties have been measured so far at NIST. (See http://properties.nist.gov/fluidsci/semiprop .) Workshop participants suggested also the following gases: $C_5F_8$, $N_2H_4$, HF, $SiCl_2$, $SiCl_3$, $SiCl_4$.

## 2. Which liquid precursors should be measured?

Some precursors have been used for many years and have well characterized physical properties. One example is tetraethyl orthosilicate (TEOS), which could be used to demonstrate NIST's ability to measure the vapor pressure of a relevant liquid precursor. Other precursors, however, are poorly characterized because they were only recently created or identified as candidates to solve new technical needs. For example, to create just one high dielectric material, hafnium oxide, researchers at a recent conference reported using hafnium nitrate, hafnium chloride, tetrakis-dimethylamino hafnium, and tetrakis-dimethylamino hafnium [1].

Such a lack of consensus among researchers and perhaps the proprietary concerns of precursor manufacturers complicate the selection of new precursors that are relevant but poorly characterized. Several participants suggested that NIST address this difficulty by first measuring the example precursors named by the SEMI task force on precursor specifications (Liquid Chemicals committee / Europe). (See the agenda for the 12 April 2005 meeting posted at http://wps2a.semi.org/wps/portal/_pagr/118/_pa.118/123?dFormat=application/msword&docName=P033616) The following table lists some of those examples, and a broader range of precursor examples is listed in the supplementary table of precursors attached to the 2005 edition of the ITRS [2].

| formula | acronym | CAS number | use |
|---|---|---|---|
| $Si(CH_3)_3H$ | Z3MS | 993-07-7 | low $\kappa$ dielectric |
| $Si(CH_3O)_2(CH_3)_2$ | DMDMOS | 1112-39-6 | low $\kappa$ dielectric |
| $Ti\ [(CH_3)_2N]_4$ | TDMAT | 3275-24-9 | TiN barrier |
| $Al\ (CH_3)_3$ | TMA | 75-24-1 | high $\kappa$ dielectric |
| $Hf\ [(CH_3)_2N]_4$ | TDMAH | 19962-11-9 | high $\kappa$ dielectric |
| $Ta\ [N(C_2H_5)_2]_3NC(CH_3)_3$ | TBTDET | 169896-41-7 | TaN barrier |
| $Gd\ [N(Si(CH_3)_3)_2]_3$ | Gd silylamide | | high $\kappa$ dielectric |
| $Y\ (C_{11}H_{19}O_2)_3$ | Y(thd)3 | 15632-39-0 | ferroelectric |

The purities of available samples will influence which precursors are chosen for measurement. One participant pointed out the importance of solid precursors.

## 3. What properties of liquid precursors are most important?

The device that delivers a gas into a semiconductor process chamber is usually a thermal mass flow controller (MFC). Several companies have developed sophisticated MFC device models that require knowledge of the gas's heat capacity and, to a lesser extent, other properties such as thermal conductivity, equation of state, and viscosity. In contrast, the methods for delivering a liquid precursor's vapor are more diverse. They include bubbling a carrier gas through the heated liquid, injecting the liquid, either pure or mixed with a solvent, onto a hot surface, or spraying the liquid directly into vacuum or into a hot carrier gas. Several participants expected flash evaporators to become increasingly more common than bubblers. At least one participant expressed a need for improved models of vapor delivery devices, which are not as well developed as those for MFCs.

Participants said that the properties listed in the workshop's introduction were a good start. That list, with additions and other comments by participants, is given below.

*Vapor pressure*

Vapor pressure is the most important property for all vapor delivery devices. Vapor pressure data to temperatures as low as 0 °C would be useful because evaporative cooling can occur within bubblers. Several participants mentioned the importance of avoiding systematic errors due to the presence of decomposition products, dissolved gases, and other impurities.

*Thermal stability*

Knowing a precursor's decomposition rate as a function of temperature allows one to optimize the operating temperature of the delivery device. Measurements at room temperature would be useful for estimating the precursor's shelf life. Mass spectrometry and thermogravimetric analysis were mentioned as candidate techniques.

*Liquid viscosity*

Liquid viscosity affects the performance of vapor delivery devices only mildly, so an uncertainty as large as a factor of 2 may be tolerable.

*Materials compatibility*
The compatibility of precursors with materials used in the delivery system and reaction chamber is important. This is a concern of the SEMI task force on stainless steel and surface analysis specifications (Gases Committee / North America).

*Other properties*

| | |
|---|---|
| Surface tension | Formation of bubbles and drops, spreading of drops on surfaces |
| Wetting angle | Spreading of drops on surfaces (sessile drop technique suggested) |
| Liquid density | Estimation of liquid volume from mass measurements |
| Heat of vaporization | Droplet evolution |
| Physisorption | Precursor purging during an ALD cycle (atomic layer deposition) |
| Vapor diffusion | Kinetics near the reaction surface |

## 4. Are the data efficiently available?

The existing NIST data on the properties of semiconductor gases need better advertising. A show of hands demonstrated that none of the non-NIST workshop participants know of the NIST page of gas property data at http://properties.nist.gov/fluidsci/semiprop. Suggestions for improvement included the following.

- Create an entry point to the above web page at the NIST level. (Adding a link from http://www.nist.gov/srd/fluids.htm seems the simplest way to do this.)
- Add a link from the SEMI website.
- Advertise better the NIST work at meetings such as Semicon West.

## References

[1] *CMOS Front-End Materials and Process Technology*, Materials Research Society symposium proceedings volume 765, edited by T.-J. King, B. Yu, R.J.P. Lander, and S. Saito (MRS, Warrendale, Pennsylvania, USA, 2003).

[2] “Yield Enhancement”, *International Technology Roadmap for Semiconductors*, 2005 edition.

## Appendix A

### Semiconductor gases measured by NIST

The data for some gases are not yet published. The published data are available at http://properties.nist.gov/fluidsci/semiprop/ and in the journal articles listed after the table.

* denotes unpublished results

| | | viscosity | | speed of sound | |
|---|---|---|---|---|---|
| **formula** | **name** | **temperature (K)** | **pressure (kPa)** | **temperature (K)** | **pressure (kPa)** |
| $SF_6$ | sulfur hexafluoride | 298.15 | 1700 | 230 - 460 | 1500 |
| $CF_4$ | carbon tetrafluoride | 200 - 400 | 3400 | 300 - 475 | 1500 |
| $C_2F_6$ | perfluoroethane | 225 - 375 | 3100 | 210 - 475 | 1500 |
| $Cl_2$ | chlorine | 300 - 400 | 3300 | 260 - 440 | 1500 |
| $H_2^*$ | hydrogen | 225 - 400 | 3300 | | |
| $O_2^*$ | oxygen | 225 – 400 | 3300 | | |
| $N_2$ | nitrogen | 298.15 | 3400 | | |
| He | helium | 298.15 | 3400 | | |
| $NF_3$ | nitrogen trifluoride | 225 - 375 | 3400 | 200 - 425 | 1600 |
| $Ga(CH_3)_3$ | trimethyl gallium | | | 340 - 420 | 900 |
| NO | nitric oxide | | | 200 - 425 | 1500 |
| $CH_4$ | methane | 293.15 | 3300 | | |
| $C_3H_8$ | propane | 293 - 373 | 3400 | | |
| $N_2O$ | nitrous oxide | 200 - 375 | 3400 | 220 - 460 | 1600 |
| Ar | argon | 225 - 373 | 3400 | | |
| $HBr^*$ | hydrogen bromide | 250 - 400 | 3000 | 230 - 475 | 1500 |
| $BCl_3^*$ | boron trichloride | 300 - 400 | 1300 | 300 - 460 | 1500 |
| $WF_6$ | tungsten hexafluoride | | | 290 - 420 | 300 |
| $C_2H_4O$ | ethylene oxide | | | 285 - 440 | 1000 |
| $C_4F_8^*$ | octofluorocyclobutane | 300 - 375 | 1600 | | |
| $CO^*$ | carbon monoxide | 225 - 375 | 2500 | | |
| $CO_2^*$ | carbon dioxide | 225 – 375 | 2500 | | |
| $NH_3^*$ | ammonia | 300 - 375 | 3500 | | |
| $SiF_4^*$ | silicon tetrafluoride | 215 – 375 | 2500 | | |

**Journal articles**


1. 'Viscosity and speed of sound of gaseous nitrous oxide and nitrogen trifluoride measured with a Greenspan viscometer', Hurly, JJ, Int. J. Thermophys. 25, 625-641 (2004).
2. 'The viscosity of seven gases measured with a Greenspan viscometer', Hurly, JJ; Gillis, KA; Mehl, JB; Moldover, MR, Int. J. Thermophys. 24, 1441-1474 (2003).
3. 'Thermodynamic properties of gaseous nitrous oxide and nitric oxide from speed-of-sound measurements', Hurly, JJ, Int. J. Thermophys. 24, 1611-1635 (2003).
4. 'Thermophysical properties of chlorine from speed-of-sound measurements', Hurly, JJ, Int. J. Thermophys. 23, 455-475 (2002).

5. 'Thermophysical properties of nitrogen trifluoride, ethylene oxide, and trimethyl gallium from speed-of-sound measurements', Hurly, JJ, Int. J. Thermophys. 23, 667-696 (2002).
6. 'Ab initio values of the thermophysical properties of helium as standards', Hurly, JJ; Moldover, MR, J. Res. NIST 105, 667-688 (2000).
7. 'Thermophysical properties of gaseous HBr and BCl3 from speed-of-sound measurements', Hurly, JJ, Int. J. Thermophys. 21, 805-829 (2000).
8. 'Thermodynamic properties of sulfur hexafluoride', Hurly, JJ; Defibaugh, DR; Moldover, MR, Int. J. Thermophys. 21, 739-765 (2000).
9. 'Thermophysical properties of gaseous tungsten hexafluoride from speed-of-sound measurements', Hurly, JJ, Int. J. Thermophys. 21, 185-206 (2000).
10. 'Thermophysical properties of gaseous CF4 and C2F6 from speed-of-sound measurements', Hurly, JJ, Int. J. Thermophys. 20, 455-484 (1999).

## Appendix B

### Tasks specified by the 2000 NIST workshop on mass flow control for the semiconductor industry

**Workshop report (contact Berg)**
*Workshop on Mass Flow Measurement and Control for the Semiconductor Industry*,
R.F. Berg, D.S. Green, and G.E. Mattingly, NIST Special Publication 400-101 (2001).

**Summary article (http://www.future-fab.com/documents.asp?d_ID=1169)**
*Mass flow research and standards: NIST workshop results*,
R.F. Berg, D.S. Green, and G.E. Mattingly, *Future Fab* **10**, 235-238 (2001).

The seven chief recommendations of the 2000 workshop are listed in the table below; two are concerned with gas properties.

| Task specified in 2000 | Institution | Outcomes 2000 - 2005 |
|---|---|---|
| Devise a technique to verify MFC performance that is independent of the process chamber. | none specified | New commercial devices. |
| Characterize the performance of each new MFC with nitrogen as well as with its nameplate gas. | MFC manufacturers | N2 characterization done by at least some companies. |
| Increase the range of transfer standards for conducting round-robin tests (0.01 sccm to 1000 slm). | **NIST** | Quartz capillaries, molblocs, and sonic nozzles: 0.1 sccm to 260 slm (6.4 out of the 8 decades specified) |
| Improve the primary (0.025%) and transfer (0.1%) standards for gas flow. | **NIST** | Primary standards: 0.02 %<br>Transfer standard: 0.04 % |
| Expand and reprioritize the list of gases to be studied. Schedule and conduct property measurements. | **NIST** | $WF_6$, HBr, $BCl_3$, $CL_2$, $C_2H_4O$, $Ga(CH_3)_3$, Ar, $CH_4$, $C_3H_8$, $N_2$, $SF_6$, $CF_4$, $C_2F_6$, NO, $N_2O$, NF3 |
| Establish and maintain a public, Web-based database of gas properties. | **NIST** | 49 gases listed in properties.nist.gov/fluidsci/semiprop/ |
| Develop metrology to characterize liquid flow controllers. | **NIST** | |