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Modeling the characteristics of
gas system dry-down

OVERVIEW This article examines techniques and theoretical modeling for determining the suitability — particularly “dry-down” behavior — of different types of materials for the construction of gas distribution systems in a semiconductor manufacturing facility. The tested material includes stainless steel and carbon steel tubes and pipes with various surface finishes. These tests also include a straightforward approach for evaluating gas system valves, which are otherwise difficult to evaluate, with an equivalent piece of pipe that has a similar dry-down behavior. Results illustrate a strong temperature effect on outgassing of materials that have rough surface finishes.

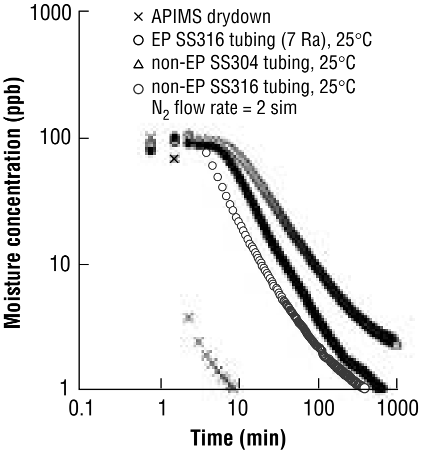

Figure 1. Dry-down characteristics EP SS316 (7 Ra), non-EP SS316, and non-EP SS304 tubing samples, all at 25°C with a 2 slm N_2 flow rate, and the APIMS dry-down characteristics.

Construction costs of gas distribution systems have escalated significantly with the demand for impurity levels <1 ppb in electronics bulk gases. Typical impurities of interest are H_2O, CO_2, O_2, and CH_4. Among these, moisture receives the most attention because it is relatively difficult to remove from a gas distribution system. Therefore, the moisture dry-down characteristic is an important factor in the selection of construction materials that have an impact on cost and scheduling.

Material selection is often based on previous experiences or the best components commercially available. Because this is not always the best approach, several theoretical models have been developed in recent years [1–3] to aid in the selection of appropriate construction materials and to predict the characteristics of the gas distribution system. For example, we previously developed the DryCom theoretical model to predict moisture dry-down time of gas distribution systems [3] (see “The DryCom model” on page 126). This model requires an isotherm for each type of material; an isotherm is an experimental value that can be deduced from a dry-down curve of the material.

Previously, we verified the integrity and accuracy of the DryCom model using small gas distribution systems [4]. To further enhance the capability of this model, we have now measured isotherms and outgassing characteristics for stainless steel (SS) tubes and pipes with different surface finishes, as they are often used in gas distribution systems.

In recent work, we have also addressed valves used in the construction of gas distribution systems. It is difficult to calculate the internal surface area of valves because of the complexity of their configurations, but the surface area is an important parameter in the calculation of dry-down time. Furthermore, valves are composed of several materials, such as elastomers and SS, that make theoretical simulation of their dry-down behavior very complicated.

Our reasoning is that it is simpler to replace the valve with an equivalent piece of SS pipe, which has the same dry-down time as a valve, in any calculation. Using this approach has enabled us to model gas distribution systems realistically.

Most of a gas distribution system used in a semiconductor manufacturing facility is located inside a climate-controlled building. However, a portion of the system may be exposed to ambient air where the surrounding temperature can vary drastically due to

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Table 1. Materials tested *

Test material	Size (OD inches)	Surface finish (manufacturing spec)	Measured surface roughness (µin)
SS 316 (tube)	0.5	EP 7 Ra	7
SS 316 (tube)	0.5	BA (no specification)	12.84*
SS 304 (tube)	0.5	BA (no specification)	27.83*
SS 304 (seamless pipe)	0.25 (Sch 40)	SA312	32.7
Carbon steel (CS)	0.25 (Sch 40)	A-106	23
Diaphragm valve	0.125	not applicable	not applicable
Diaphragm valve	0.5	not applicable	not applicable

*Determined by profilometry

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The DryCom model

The DryCom model gas distribution system is divided into a series of well-mixed tanks [5]. Two sets of equations can be applied for each tank. One set is used when the amount of adsorbed moisture exceeds a monolayer and the water is physisorbed on top of other layers of water. In this case, we can write a mass balance equation for the bulk gas phase as

$$V_r \frac{dc_i}{dt} = Q(c_{i-1} - c_i) - A_r k_g (c_i - c_i^*) \qquad (1)$$

where V_r is the tank volume, c_l is the bulk moisture concentration in the l^{th} tank, t is time, Q is the volumetric flow rate, c_{i-1} is the bulk moisture concentration in the $(i-1)^{st}$ tank, A^r is the tank surface area, k_g is the mass transfer coefficient, and c_l^* is the moisture concentration at the gas side of the gas-stainless steel interface. The mass transfer coefficient k_g can be determined from mass transfer correlations for laminar or turbulent flows [6].

In the physisorbed regime, we assume that the adsorbed-phase moisture concentration q_l in the l^{th} tank is in equilibrium with c_l^*. Thus, the mass balance in the adsorbed phase can be expressed as

$$\frac{dc_i^*}{dt} = \frac{k_g(c_i - c_i^*)}{(\partial q_i / \partial c_i^*)} \qquad (2)$$

where $\partial q_i / \partial c_i^*$ is determined by taking the derivative with respect to c_l^* of the BET isotherm

$$q = \frac{q_{m1} b (P / P_{sat})}{(1 - P / P_{sat})(1 - P / P_{sat} + bP / P_{sat})} \qquad (3)$$

where q is the amount of adsorbed moisture, $P(=c_l^* RT)$ is the water vapor pressure, P_{sat} is the saturation vapor pressure of water, and q_{m1} and b are adsorption parameters.

The second set of equations is used when the adsorbed moisture is less than one monolayer and the moisture is chemisorbed onto the stainless steel surface. The bulk gas-phase balance is the same as that for the physisorbed case

$$V_r \frac{dc_i}{dt} = Q(c_{i-1} - c_i) - A_r k_g (c_i - c_i^*) \qquad (4)$$

In the chemisorbed regime, the interfacial moisture concentration in the gas phase c_l^* is not in equilibrium with the chemisorbed moisture. Thus, a separate balance is written for the interfacial gas phase. The balance accounts for the dissociation of the H_2O into H and OH groups by squaring the adsorbed moisture terms.

$$V_r \frac{dc_i^*}{dt} = A_r k_g (c_i - c_i^*) - A_r [k_{ads} c_i^* (1 - \theta_i)^2 - k_{des} \theta_i^2] \qquad (5)$$

where k_{ads} is the water adsorption rate constant onto stainless steel, θ_l is the fractional loading of moisture on the stainless steel, and k_{des} is the water desorption rate constant from stainless steel.

In this second set of equations, a third mass balance is expressed for the adsorbent phase.

$$q_{m2} \frac{d\theta_i}{dt} = k_{ads} c_i^* (1 - \theta_i)^2 - k_{des} \theta_i^2 \qquad (6)$$

where q_{m2} is an adsorption parameter.

These equations have been adapted for use on a graphical-user interface that can be operated on a stand-alone PC. Simulation run times are on the order of seconds. ■

seasonal and diurnal changes. Because temperature has a significant effect on dry-down behavior and outgassing of materials, the associated quality of bulk gas may be altered, especially its levels of trace impurities. Thus, to study the effect of temperature on the outgassing of materials, we measured the levels of trace impurities from 20–35°C.

The test setup

In our experiments, we submerged 20-ft test samples — made from tubes or pipes of various materials (Table 1) — in a heated bath to regulate temperature during the experiment. Surface roughness of electropolished (EP) tubing is normally specified by the manufacturer. Non-EP tubing is referred to as bright anneal (BA) without a specification of surface roughness. We therefore measured the surface roughness of the non-EP tubing with profilometry.

We used purified nitrogen (N_2) as the dry gas. We measured moisture with an atmospheric pressure ionization mass spectrometer (APIMS). Moisture content in the dry gas was <0.2 ppb. Although the APIMS dries very rapidly, the experimental error caused by the contribution from its dry-down is inevitable. It is difficult to alter the dry-down time of the APIMS, but we increased the dry-down time of the test sample by using a very low flow rate of the dry gas. Therefore, the contribution from the dry-down time of the APIMS was

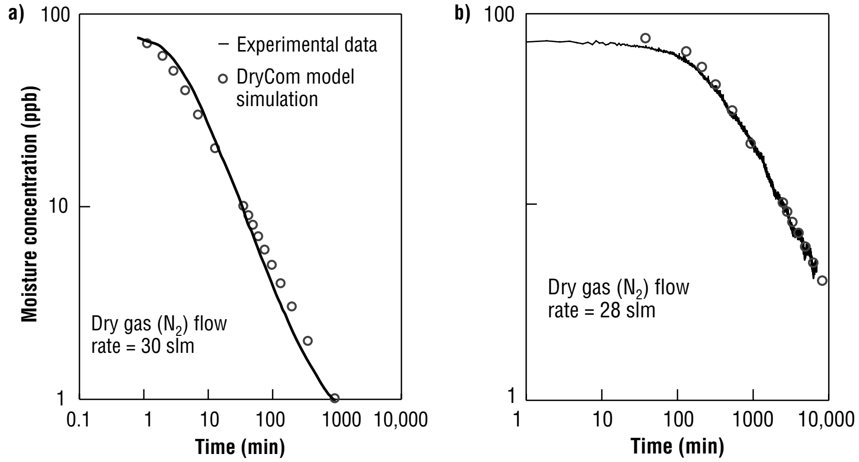

Figure 2. Dry-down behavior of **a)** SS304 and **b)** CS pipe presented with model simulation for each, all at 25°C with a 2 slm N_2 flow rate.

Table 2. Summary of isotherms for various types of materials at 25°C

Material	Parameter q_{m2} (mol/cm^2)	Parameter K (K_{ads}/k_{des} in 1/atm)
SS 316 tube (5 Ra)	8.3×10^{-11}	5.0×10^{5}
SS316 tube (7 Ra)	8.0×10^{-11}	3.5×10^{8}
SS316 tube (BA)	1.5×10^{-10}	1×10^{8}
SS304 tube (BA)	1.0×10^{-8}	2.7×10^{11}
SS304 pipe (seamless)	1.0×10^{-8}	1.0×10^{10}
Carbon steel pipe	5.0×10^{-7}	5.0×10^{8}

small with respect to that of the test sample. The flow rate of dry gas was typically maintained at 2 slm, which is slightly higher than the required gas flow rate for the APIMS.

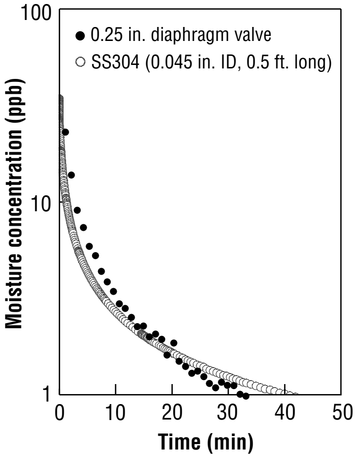

Figure 3. Moisture dry-down characteristics of a 0.25-in. diaphragm valve and its pipe equivalent.

We established the initial moisture level of the sample by introducing a known moisture standard, generated with a permeation tube, into the sample. After the sample was in equilibrium with the gas mixture, the addition of the moisture standard was terminated and the test sample immediately underwent the dry-down process. The gas exiting from the test sample was continuously monitored by the APIMS. We maintained the pressure inside the sample at a preset value during the wetting and drying process. For comparison purposes and simplification of the calculation, the experimental conditions, such as temperature, pressure, and length of the tube, remained the same for all test samples.

Tubing dry-down and isotherms

Figure 1 compares the dry-down characteristics of our EP SS316 (7 Ra), non-EP SS 316, and non-EP SS 304 samples, plotted with dry-down characteristics of APIMS. The APIMS data verifies that its dry-down time is insignificant with respect to the dry-down time of test samples; the APIMS dried very quickly and represented <3% of the dry-down time of the sample. The experimental results show that the EP SS316 (7 Ra) tube has the shortest dry-down time followed by non-EP SS316 and non-EP SS304. The dry-down time of these tubing materials becomes longer as the roughness of the internal surface increases.

It is uncommon to use piping material in gas distribution systems inside the semiconductor manufacturing facility. However, because of cost, piping would be preferred over tubing in the construction of a very large-scale gas distribution system, such as the pipeline in an industrial park. A less expensive material, such as SS304 or carbon steel (CS) pipe, is often chosen for a very large gas distribution system.

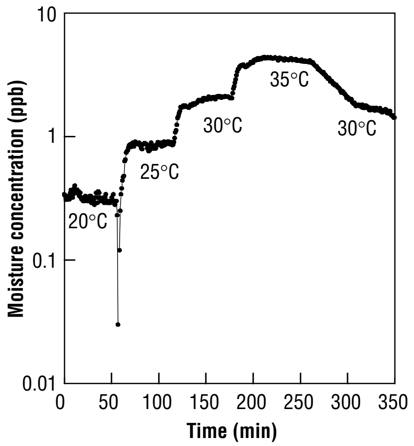

Figure 4. Change in moisture concentration as a function of ambient temperature for non-EP SS316 tubing.

To extend the application of the DryCom model to large systems, we explored the dry-down characteristics of two types of piping material: SS304 (cold draw) and CS (Fig. 2). Here, we used a much higher flow rate of dry gas because pipe dries very slowly. The data presented in Fig. 2 show that measured dry-downs agree reasonably well with the model simulation for both SS304 and CS.

One of the experimental parameters needed for each material in DryCom is the isotherm. The isotherm can be deduced from curve fitting of the dry-down characteristic for each material, as was done with the data shown in Fig. 2. From such curve fits, we obtained isotherm parameters in the chemisorbed regime for six materials (Table 2).

The parameter q_{m2} represents how much moisture is adsorbed at monolayer coverage. Not surprisingly, materials that take longer to dry down have larger q_{m2} values.

The parameter K represents the ratio of the adsorption rate constant to the desorption rate constant for that given material. Thus, while the 5Ra and the 7Ra materials have similar q_{m2} values, the slower dry down of the 7Ra is theoretically captured in a larger K value.

By using the DryCom model and the appropriate isotherms, we can estimate the dry-down time of a gas distribution system under a given operating condition.

For our investigation of two diaphragm valves, we estimated the dimensions of an equivalent piece of SS304 pipe based on experimentally determined dry-down times and the DryCom model. We found that the dry-down curve of the SS304 pipes matches that of the valves with <25% error (one example is shown in Fig. 3). It is, however, difficult to calculate an exact match for the valves because they contain several types of materials and have small dead volumes.

Effect of ambient temperature

Ambient temperature has a significant effect on the dry-down behavior of components. A higher temperature causes greater desorption of moisture from the surface of the components. As a result, more moisture molecules are released from the surface and carried away by the flowing bulk gas. This results in a higher moisture concentration in the bulk gas.

In our test to verify this, we repeatedly demonstrated an increase in moisture level of the gas exiting from the test material as ambient temperature rises (one example is shown in Fig. 4). We also found that this temperature effect becomes more pronounced as the surface roughness of a material increases. The ambient temperature has less effect on outgassing from the 0.125-in. valve than the 0.5-in. valve. The temperature effect may be related to the surface finish of the valves. For example, the internal surface finish of the small valve is 7 Ra compared to 10 Ra for the large valve. Moreover, the large valve may have more elastomer material than the small one.

Conclusion

We have found that the combination of our DryCom model and isotherms used to evaluate various tubing and pipe materials provides an understanding of moisture transport phenomena inside the gas distribution system. We can routinely use the model to predict the dry-down time of gas distribution systems as well as simulate their dry-down characteristics. This approach is very useful in selecting the most cost-effective material for the construction of a gas distribution system.

The dry-down curves indicate that there is no significant difference among the EP SS316 tubing. EP SS tubing dries down slightly faster than non-EP SS tubing, so the use of the best EP SS tubing (5Ra) in the gas distribution system may not be necessary. The experimental data also suggest that the SS tubes tested in this experiment are capable of delivering gas with <1 ppb of H_2O at a temperature below 25°C. Therefore, a significant cost reduction could be realized by using lower-grade materials, such as non-EP SS316 tube. Care should be taken when a large fluctuation of ambient temperature is inevitable. The data demonstrate that temperature plays an important role in the outgassing of materials, resulting in changes in impurity levels in the bulk gas. ■

Acknowledgments

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References

1. K.L. Siefering, W.H. Whitlock, J. Vac. Sci. Technol. A 5, 2685, 1994.
2. M.J. Kobus, G.H. Leggett, Microcontamination Proceedings, 212, 1993.
3. R. Ciotti, et al., *Semicon. Fabtech. 6th Ed.*, 197, 1997.
4. S. Dheandhanoo, et al., *J. IEST,* 33, March 1998.
5. O. Levenspiel, *Chemical Reaction Engineering,* 2nd ed., Wiley, New York, 1972.
6. C.O. Bennett, J.E. Myers, Momentum, Heat and Mass Transfer, 3rd ed., McGraw-Hill, New York, 1982.

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