Effect of purge pressure on desorbing water removal rate

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The need for a high purity gas supply for vacuum systems and related processing equipment has driven the requirements for the design and operation of components in gas delivery subsystems. Water has been widely regarded as a major contaminant species in such subsystems. For designs that follow generally accepted practices for construction, sealing, and layout, the primary cause of water contamination is associated with ambient atmospheric exposure during maintenance or repair. The subsequent removal of this adsorbed water, and in particular, how this process can be accelerated has been the subject of much interest. While the enhancement of molecular desorption through various methods has received considerable attention, the effective removal of water vapor after desorption is also worthy of attention. This is especially true when considering the typical geometry of gas distribution and delivery subsystems. It is shown that at typical purge pressures, a water molecule desorbing from a surface is likely to be adsorbed again. Thus, desorption may be required multiple times for the molecule to be removed from the subsystem. However, if the purge flow is operated at modest vacuum, the desorbing molecule remains in the purge stream considerably longer and travels farther downstream before being readsorbed; thus improving the removal rate. The primary focus of this investigation is to understand the dependence of the rate of water removal on the pressure of an inert gas purge. In most cases, the implementation of lower pressure purge may be accomplished with little or no change to existing equipment. In addition to the obvious savings and convenience resulting from a time reduction, considerably less purge gas is consumed. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1735844]

I. INTRODUCTION

Many vacuum processes typically used in surface science, semiconductor manufacturing, and related fields require the delivery of high-purity gasses to a process chamber. Etch, chemical vapor deposition, and related processes routinely employ gasses that are highly reactive and readily form undesirable compounds when exposed to even trace levels of contamination. In other cases such as aluminum physical vapor deposition, the presence of contamination can adversely affect critical aspects of the resulting film. In a semiconductor manufacturing facility these contamination issues are a significant economic factor.[1,2] Of the many contaminant species, water is considered the most troublesome. Delivery components and subsystem designs have been the focus of many studies recently, as have the many methods used to clean and condition the wetted surfaces of these and other components.[3–6] While most modern, high-purity gas delivery subsystems are designed to minimize internal sources of common contaminants, the exposure of the wetted surfaces to ambient atmosphere remains a major source of water contamination. Even brief atmospheric exposure allows monolayer water coverage on internal surfaces.[7,8] With a surface residence time of approximately 1 day, water contamination becomes the impediment to a rapid return to a process-ready condition.

The challenge of effective removal of adsorbed water from gas delivery subsystems is considerably different from that encountered for a large vacuum vessel. First, the prospect of baking the subsystem to promote rapid desorption is impractical. Other techniques requiring line-of-sight to all surfaces are ineffective due to the internal geometry of the subsystem. In addition to the difficulties of enhancing water desorption, the internal geometry prevents effective removal of the desorbed vapor. With length-to-radius ratios of typically 100–1000 in such a system, a water molecule is desorbed and readsorbed numerous times in the process of being entirely removed.

The opportunity to improve purging effectiveness by enhancing the vapor transport of the contaminant species is worthy of attention and the common practice of purging at high pressure requires critical review.

II. MATHEMATICAL MODEL

To analyze the removal of water contamination from gas delivery lines and components, a model representing the primary mechanisms involved is developed. Assumptions consistent with the physical conditions are made to facilitate the solution. A governing differential equation for the molar density of the water vapor within a cylindrical pipe is derived. An adsorption/desorption relation for submonolayer water on stainless steel determines the boundary condition for the molar density at the tube wall.

A. Assumptions

The model assumes a cylindrical shape representing commonly used 1/4 in. stainless steel tubing (inner diameter 0.46 cm) having a tube length of at least 50 diameters. The purge gas is nitrogen in the viscous regime, characterized with a

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fully developed laminar profile. The purge gas volumetric flow provides sufficient average velocity such that the axial transport is considerably more than that of diffusion. The residence time for a water molecule adsorbed on the wall is 10^5 s and the molar surface density for a monolayer is 1.7 $\times 10^{-5}$ mol/m^2. The diffusion coefficient for water vapor in nitrogen at 1 atm and 20 °C is taken to be 2.5×10^{-5} m^2/s. The diffusion coefficient varies inversely with pressure—valid while the nitrogen flow regime is viscous.

B. Governing equation for molar density

The derivation of the governing equation for the molar density function within the tube involves two transfer mechanisms: diffusion and purge gas velocity. The flux of water vapor is effected by the gradient of the molar density (diffusive) and by the purge flow (convective), as shown by

$$\mathbf{j}=-D\nabla n(\rho,z)+\boldsymbol{\nu}(\rho)n(\rho,z), \tag{1}$$

where $\mathbf{j}$ is the molar flux, D is the coefficient of diffusion, $n(\rho,z)$ is the molar density function, and $\boldsymbol{\nu}(\rho)$ is the velocity of the purge gas as a function of radius. Once in the volume of the tube, it can be assumed that no dissociation or formation occurs, so the total molar number is conserved. This leads to the condition

$$\nabla\cdot\mathbf{j}=-\frac{\partial n(\rho,z)}{\partial t} \tag{2}$$

and is further reduced in the case of steady state by setting the right-hand side to zero. Combining Eqs. (1) and (2), and considering the symmetry of the problem, the steady state result becomes

$$\frac{D}{\rho}\frac{\partial}{\partial r}\left[\rho\frac{\partial n(\rho,z)}{\partial \rho}\right]+D\frac{\partial^2 n(\rho,z)}{\partial z^2}-\nu_z\frac{\partial n(\rho,z)}{\partial z}=0 \tag{3}$$

The second term in Eq. (3) can be neglected due to the axial transport assumption earlier. Since the purge flow is fully developed, the axial component of the velocity ν_z is

$$\nu_z=\frac{3Q_V}{\pi R^2}\left(1-\frac{\rho^2}{R^2}\right), \tag{4}$$

where Q_V is the volumetric purge flow, and R is the inner radius. If the radial variable is scaled as a fractional radius $r=\rho/R$, Eqs. (3) and (4) can be combined as

$$\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial n(r,z)}{\partial r}\right]+\frac{3Q_V}{\pi D}(r^2-1)\frac{\partial n(r,z)}{\partial z}=0. \tag{5}$$

Equation (5) is the governing equation for the molar number density. This form is somewhat analogous to the well-studied thermal transfer problem.[9] However, the two problems are different in the way that thermal conductivity and diffusion coefficient vary with pressure. Examination of Eq. (5) yields the following notable features and scaling properties:

- It is independent of the inner radius of the tube R, however, some of the underlying assumptions require limits on R.
- Since both Q_ν and D are inversely proportional to pressure, it is independent of the purge gas pressure for a constant mass flow of purge gas.
- It can be reduced to two ordinary differential equations using the technique of separation of variables $n(r,z)=n(r)n(z)$ for certain cases of boundary conditions.

C. Boundary conditions

The condition for $n(r,z)$ at the inlet boundary is set to represent a practical situation where the purge gas has fixed moisture contribution which becomes an additive constant to the solution. It will be set to zero for mathematical convenience. The boundary condition at the wall is determined by setting the net molar flux equal to the difference in adsorption and desorption on the surface. A relatively straightforward model of this behavior is employed. For submonolayer coverage, the adsorption is a product of the arrival rate, the number of available sites, and the sticking probability. The desorption rate is proportional to the number of moles on the surface divided by the residence time. Thus

$$\mathbf{j}|_{r=1}=\left[\frac{1}{4}\langle\nu\rangle S(1-\theta)n(r,z)|_{r=1}\right]-\left[\frac{N_0\theta}{\tau}\right],$$

where $\langle\nu\rangle$ is the average thermal velocity of a water molecule, S is the sticking probability, θ is the coverage, N_0 is the monolayer molar surface density, and τ is the residence time. At $r=1$, diffusion is the only transport mechanism, so the flux at the wall is related to the gradient in density as

$$\mathbf{j}|_{r=1}=-D\left.\frac{\partial n(r,z)}{\partial r}\right|_{r=1}.$$

This enables the boundary condition at the wall to be expressed as

$$D\left.\frac{\partial n(r,z)}{\partial r}\right|_{r=1}=\left[\frac{N_0\theta}{\tau}\right]-\left[\frac{1}{4}\langle\nu\rangle S(1-\theta)n(r,z)|_{r=1}\right]. \tag{6}$$

Worth noting is that at full monolayer coverage ($\theta=1$), the adsorption term is zero and the flux of water at the surface is independent of the molar density in the gas. As the coverage decreases, the adsorption term becomes more significant—decreasing the flux from the surface, and hence, the removal rate. This adsorption factor is proportional to the local molar density, which in turn is dependent on the purge gas parameters.

The emphasis of this analysis is on the removal of submonolayer coverage. This focus is justified given that:

- Since the residence time for water-on-water is $\sim 10^{-5}$ s while that of water-on-stainless steel is $\sim 10^5$ s, the net flux of water from the surface is significantly lower during the removal of the last monolayer compared with that for the bulk.
- Since no appreciable adsorption takes place until the water achieves submonolayer coverage, the purge gas parameters have little effect on the flux in a bulk coverage condition.

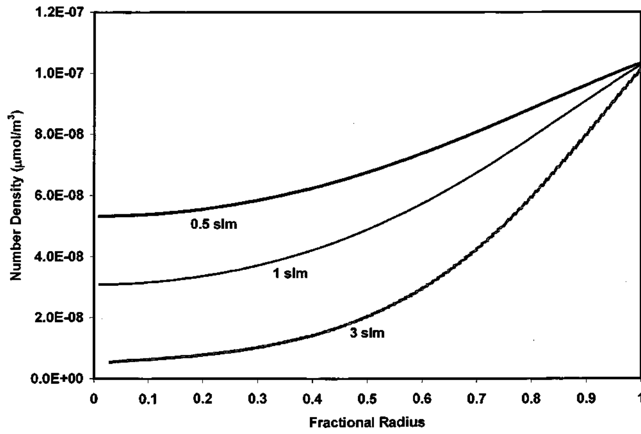

FIG. 1. Molar density profile for various purge gas mass flow rates with the following conditions: $P = 1$ atm, $\theta = 0.9$, and $S = 0.0001$.

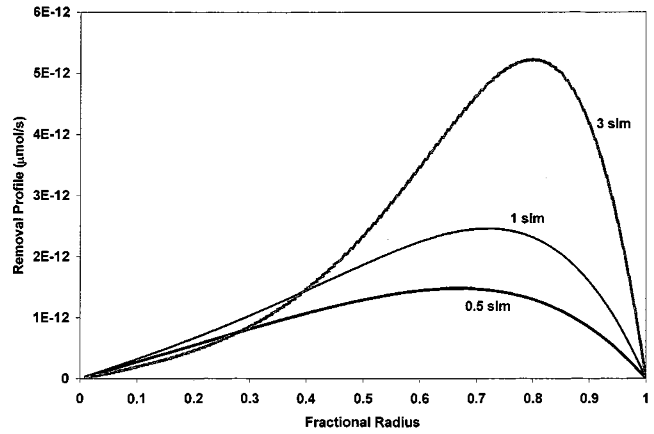

FIG. 2. Removal rate profile for various purge gas mass flow rates with the following conditions: $P = 1$ atm, $\theta = 0.9$, and $S = 0.0001$.

D. Removal rate

The removal rate is defined as the number of moles leaving the tube per unit of time. It is calculated by integrating the product of the molar density and the purge velocity over the surface of the tube exit. This is given by

$$\Phi = 6 Q_v \int_0^1 n(r)(r - r^3) dr. \tag{7}$$

Since the model addresses the steady state condition, removal rate is a useful metric to evaluate the effectiveness of the purge gas parameters.

III. MODEL RESULTS

The solution to Eq. (5) with the boundary condition of Eq. (6) is solved using separation of variables to obtain an exponential form for $n(z)$ with the remaining ordinary differential equation for $n(r)$ evaluated using numerical methods. For various conditions for coverage, sticking probability, purge gas mass flow, and purge gas pressure, the molar density function is obtained.

Parametric studies of molar density $n(r)$ show general trends as expected. As θ approaches 1 or S approaches 0, the $n(r)$ becomes uniform across the radius as no readsorption is occurring. At nominal values of θ and S, as the mass flow is increased, $n(r)$ exhibits a steeper gradient across the radius as shown in Fig. (1). That is, the purge gas is "drier" at the center when at a higher flow. The pressure independence of $n(r)$ is also verified as expected.

To aid in visualizing the removal process, the integrand of Eq. (7) is plotted in Fig. (2) for the same cases as in Fig. 1. This demonstrates amount of water exiting the tube at each point along the radial direction. The interplay between: the area increasing as r^2, the purge gas velocity profile decreasing as r^2, and the molar density profile, makes for interesting comparisons between the different mass flow rates. The high mass flow case has the least amount of removal near the center, but has far more removal nearer the wall when compared to the lower mass flow rates due to the overall higher velocity.

Parametric studies of removal rate Φ, calculated numerically following Eq. (7), demonstrate its dependence on coverage, sticking probability, purge mass flow, and purge pressure. The ranges for coverage and sticking probability values are consistent with recent work.[10–12] As shown in Fig. 3, the dependence of removal rate on pressure tends to be inverse linear in a large region of the selected parameter space (where $\theta < 0.99$ and $S > 0.001$). Figure 4 also demonstrates that when adsorption becomes a significant factor at the wall boundary, the purge pressure effect becomes significant.

The effect of mass flow on the removal rate for various pressures is shown in Fig. 5. Here it can be seen that the removal rate increases with increasing flow. However, dependence becomes increasingly nonlinear as the mass flow is increased. The basis for this relation is qualitatively demonstrated in Fig. 2. Increasing the mass flow rate decreases the efficiency of the purge as the center of the stream becomes less saturated with moisture.

IV. DISCUSSION

From examining the boundary condition statement and the parametric results, it is evident that the details of the surface/water interaction (θ, τ, and S) are critical to the re-

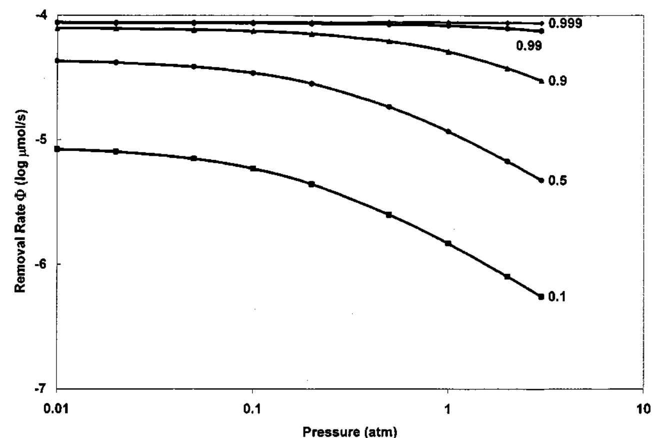

FIG. 3. Removal rate Φ vs purge gas pressure for various θ with $S = 10^{-6}$.

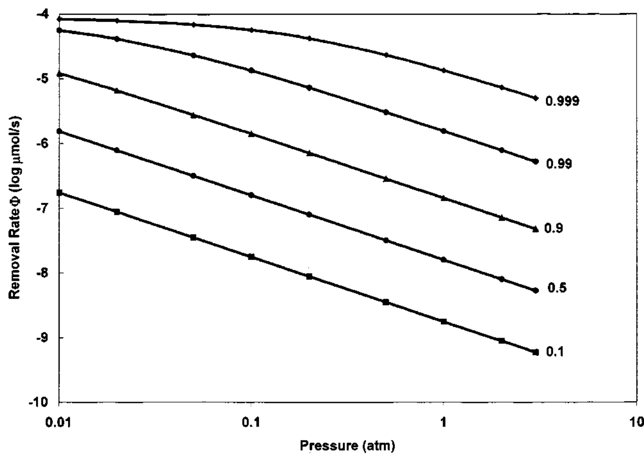

FIG. 4. Removal rate Φ vs purge gas pressure for various θ with $S=0.001$.

moval rate while purging. However, these factors are typically not controllable in a practical situation. The purge gas pressure and mass flow rate are controllable to an extent in most current designs.

A. Purge gas pressure

To maximize removal rate the optimal pressure is, practically speaking, the lowest pressure. This value is often limited by the geometry and pumping capability of the subsystem. While there is a problem if the pressure becomes too low and the flow regime transitions from viscous to molecular (where the diffusion coefficient becomes constant), this is unlikely to occur in a typical gas delivery subsystem. In fact, it is readily estimated from the Hagen–Poiseuille equation that for a 1 slm mass flow through a 1/4 in. tube, the pressure will be at 0.01 atm within a few centimeters upstream from a vacuum exit.

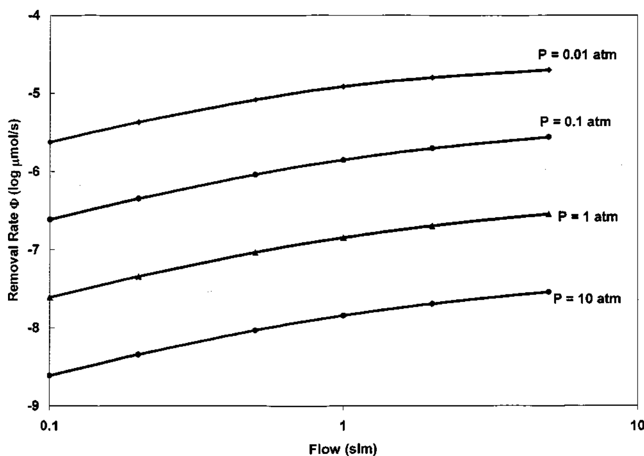

FIG. 5. Removal rate Φ vs purge gas flow rate for various pressures at $\theta=0.9$ and $S=0.001$.

B. Purge flow rate

The only quantitative consideration for optimizing purge parameters may be required when determining the mass flow rate setting. Higher mass flow settings produce a higher removal rate at the same pressure. However, increasing the mass flow increases the pressure gradient along the tube, which increases the average pressure, which in turn tends to decrease the removal rate. So for a given length and diameter tube, an optimal flow setting is expected. The ideal flow for each instance also depends on the surface conditions in the tube, which may be unknowable and dynamic during the purging process. Determining the optimal flow for a particular situation requires experimental investigation, but certainly mass flow rates in range from 0.1 to 5 slm are reasonable—both from the standpoint of removal rate and pressure gradient.

C. Purge gas purity

When considering the effectiveness of the purging process, the economics of the gas consumed is also a concern. The purge time, flow rate, and purity level each affect the cost directly. Purge time and flow rate account for the total standard liters of gas consumed; purity is a major factor in setting the cost per standard liter. Purity is typically specified as parts per million by volume concentration, but must be restated in terms of the absolute molar density to properly assess its impact. For example, if the purge gas bottle concentration is 0.1 ppm water vapor and it is used at 1 atm pressure, then the molar density it contributes is $\sim 4\times 10^{-6}$ mol/m^3. Whereas the same 0.1 ppm purity gas contributes $\sim 4\times 10^{-8}$ mol/m^3 at 0.01 atm purge pressure. In other words, since the adsorption of water at the surface depends only on the absolute molar density, not on relative concentration, the "effective purity" of the purge gas increases with decreasing purge pressure for the same volumetric flow.

D. Time to achieve acceptable moisture level

While the model presented here represents the steady state molar density and removal rate, the effect of purge gas pressure and mass flow rate can also be applied to the time dependent problem. Since the residence time of molecules adsorbed on the surface is orders of magnitude longer than both the diffusive and convective transit times, the process of adsorbed moisture removal can be considered quasisteady state. An issue of practical matter is the relative amount of time spent in bulk removal versus submonolayer removal. For many applications, it may be acceptable to perform a purge and begin operation with the last monolayer remaining. The purge pressure has little bearing on the required time to achieve this state. One the other hand, if lower contamination levels are required before returning the subsystem to operation, the time spent removing a given portion of the last monolayer is substantially longer. It is during this phase of the removal process that a lower purge pressure can dramatically reduce the required time.

E. Other purging techniques

With the understanding this model provides, it is useful to examine alternative techniques and develop new methods for more effective purging.

1. Cycle purging

A commonly employed technique for purging "dead legs" in gas delivery subsystems is called cycle purging. This approach varies the pressure, usually between several psig and rough vacuum, in a repeated pump-purge cycle. Compared with a continuous-flow purge, this technique ensures movement of purge gas throughout the system's dead legs. While there is little doubt regarding its effectiveness for the intended purpose, there have also been anecdotal accounts of improved purge performance in systems without dead leg features. One may speculate that the effectiveness of a cycle purge, especially in this case, is related to the fact that a considerable portion of the purge process is performed at low pressure, as opposed to the cycling action itself.

2. Turbulent flow purging

The model results indicate clearly that increasing the radial transport mechanism near the wall is key to improving removal. Increasing the diffusion coefficient by decreasing pressure has a dramatic effect; however, creating a turbulent flow condition would further facilitate transport near the walls. Inducing and controlling the onset of turbulence in such applications may generate enhanced purging capabilities.

F. Experimental verification of the model

The model and results presented here require experimental verification. Valid tests must be designed and performed with appropriate apparatus and instrumentation. Standard test procedures for evaluating gas delivery components specify that moisture content of the gas from the test artifact be measured at a specific pressure and mass flow rate.[13] In fact, the recommended trace analysis instruments for such testing require these conditions for proper operation. Conversely, the verification tests for this model necessitate an absolute moisture density measurement, independent of the purge gas pressure and flow conditions. Thus, a modified test procedure is required to effectively test the results of this model.

V. CONCLUSIONS

For high purity gas distribution and delivery subsystems, any maintenance operation that exposes the internal surfaces to air requires the subsequent removal of contaminant species. Depending on the design and materials of the subsystem and the level of exposure, the removal process can require hours. In a research environment, this time is at best an inconvenience. For vacuum-processing systems in a semiconductor manufacturing facility, the economic impact in terms of lost uptime, is significant.

A model for the purging process of adsorbed water is developed based on assumptions consistent with gas delivery subsystem tubing. The effect of purge pressure on the moisture removal rate is first order in the region where readsorption is an appreciable mechanism (i.e., submonolayer coverage). Lowering purge gas pressure increases both the volumetric flow and the diffusion coefficient—resulting in improved removal rate.

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