

SIMPLE MCP TRANSPORT MODEL

ANGEL YANGUAS-GIL

1. DESORPTION KINETICS IN A CYLINDRICAL PORE IN PRESENCE OF PHYSISORPTION

After the end of a dose, pores in a substrate are ideally saturated with a constant partial pressure of a reactant. During purging, this reactant needs to diffuse out of the pore. The characteristic time determines the interval between ALD doses.

In most of cases, dimensions of the pores and process pressure are such that diffusion takes place in the Knudsen regime. This allows us to estimate the characteristic diffusion times based on the Knudsen diffusion coefficient and the characteristic dimensions of the pore. In this case:

$$(1) \quad \tau_{\text{diff}} = \frac{L^2}{D} = \frac{3L^2}{v_{th}d}$$

where v_{th} is the mean (rms) thermal velocity, L is the pore length and d is the pore diameter.

However, this model assumes that there is no physisorbed species on the internal surface of the pores. The goal is to understand how the presence of weakly bonded species in equilibrium with the precursor in the gas phase can affect the outgassing process and the required purge times.

1.1. Model equation. We will assume that a fraction of the available surface sites θ is covered by physisorbed species. Then, assuming adsorption and desorption processes that are first order in the fraction of available sites and surface coverage, respectively, the change with time of the surface coverage will be given by:

$$(2) \quad \frac{d\theta}{dt} = \beta s_0 \frac{1}{4} v_{th} \frac{p}{k_B T} (1 - \theta) - k_d \theta$$

In steady-state condition this expression leads to a Langmuir isotherm:

$$(3) \quad \frac{\theta}{1 - \theta} = \frac{1}{k_d} \beta s_0 \frac{1}{4} v_{th} \frac{p}{k_B T}$$

Likewise, we can use the diffusion equation to model the transport of the gaseous species inside the feature:

$$(4) \quad \frac{\partial n}{\partial t} - D \frac{\partial^2 n}{\partial z^2} = -\frac{S}{V} \beta \frac{1}{4} v_{th} n (1 - \theta) + \frac{S}{V} \frac{k_d}{s_0} \theta$$

subject to the following boundary conditions: at the bottom of the pore (or the middle point if it is a two-sided open pore) the boundary condition is:

$$(5) \quad \left. \frac{\partial n}{\partial t} \right|_L = 0$$

At the entrance of the pore, there is a linear relationship between the density gradient and the precursor density:

$$(6) \quad -D \left. \frac{\partial n}{\partial t} \right|_0 = \frac{1}{4} v_{th} n(0)$$

The impact of physisorption on the outgassing from a pore can be studied by solving these two equations together subject to the boundary conditions mentioned above. However, it is possible to greatly simplify the problem if the surface coverage θ is small. The first thing is to realize that by combining Eqs, 4 and 2 we obtain an expression relating the rate of change of gaseous and adsorbed species:

$$(7) \quad \frac{\partial n}{\partial t} - D \frac{\partial^2 n}{\partial z^2} = -\frac{S}{s_0 V} \frac{\partial \theta}{\partial t}$$

If the coverage is small, the Langmuir isotherm 3 can be simplified, so that:

$$(8) \quad \frac{\theta}{\theta_0} = \frac{p}{p_0}$$

Finally, under the quasiequilibrium approximation (adsorption/desorption rates are much faster than diffusion rate), we obtain from Eq. 9 that:

$$(9) \quad \frac{\partial \theta}{\partial t} = \frac{\partial n}{\partial t} \frac{\theta_0}{n_0}$$

so that Eq. 4 is transformed into:

$$(10) \quad \left(1 + \frac{S}{s_0 V} \frac{\theta_0}{n_0} \right) \frac{\partial n}{\partial t} - D \frac{\partial^2 n}{\partial z^2} = 0$$

From Eq. 10 we see that the net effect of physisorption is to slow down the outgassing process, and the outgassing can be modeled using an effective diffusion coefficient D_{eff} given by:

$$(11) \quad D_{\text{eff}} = \frac{D}{1 + \frac{S}{s_0 V} \frac{\theta_0}{n_0}}$$

So that the characteristic desorption time τ_d , by analogy with 1 is given by

$$(12) \quad \tau_d = \left(1 + \theta_0 \frac{4k_B T}{p_0 s_0 d} \right) \tau_{\text{diff}}$$

where p_0 is the precursor pressure during dose time and d is the diameter of the pore.

Note. *The physisorption behavior is determined by picking an initial coverage θ_0 and pressure p_0 . These two parameters by themselves define the adsorption isotherm.*

Note. *The presence of physisorption can increase desorption times by more than two orders of magnitude. We can estimate desorption times by assuming a coverage θ_0 for a given precursor pressure p_0*

1.2. Validity of the model approximations. How good an approximation is Eq. 12? To answer this question we solved the full diffusion, adsorption/desorption model for a single MCP pore for different values of θ_0 . Figure 1 shows the outgassing flow as a function of time. When the flow is plotted against the normalized time t/τ_d all plots coalesce into a single curve, indicating that τ_d is indeed a good estimate of the characteristic time for the out-diffusion process.

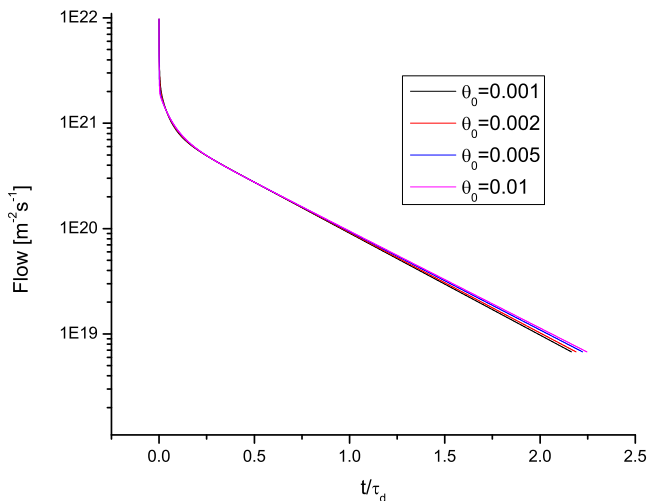


FIGURE 1. Out-diffusion flow of a single pore showing coalescence into a single curve when plotted against normalized time t/τ_d

By having physisorbed species the characteristic time can be much larger than that predicted using the pure diffusion theory. In Figure 2 the τ_d/τ_{diff} ratio is plotted against the θ_0/p_0 ratio, where the pressure is in Torr. Figure 2 shows that physisorption can have a substantial effect on the purge times of isolated pores.

2. SIMPLIFIED ADSORPTION-DESORPTION MODEL

The model developed in the previous section assumes a single, isolated pore. In this section we generalize the model and couple it to a simple model of a viscous flow reactor to understand the dynamics of purging in presence of high aspect-ratio substrates.

To be precise, we should solve the diffusion model for every point of the MCP coupled to the reactor flow. But it would take forever. Instead, we can take advantage of the

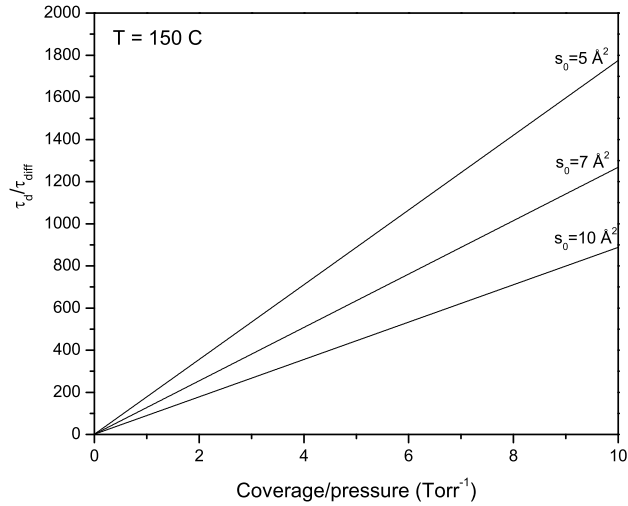


FIGURE 2. Relative increases in desorption time due to the presence of physisorbed species as a function of τ_d/τ_{diff} the θ_0/p_0 ratio for the dimensions of an MCP pore

result obtained above showing that the desorption kinetics from an MCP is dominated by a characteristic time τ_d , such as that provided in the previous section.

In order to model a more complex situation involving inflow into the pore, we just apply the superposition principle. Thus, if N is the total number of molecules inside the pore, we have that:

$$(13) \quad \frac{dN}{dt} = S_{op}\phi_{in} - \frac{1}{\tau_d}N$$

where

$$(14) \quad \phi_{in} = \frac{1}{4}v_{th}n$$

is the precursor flux at the entrance of the pore, which depend on the precursor density in the reactor n and the area of the opening of the pore, S_{op} .

If we assume a surface coverage θ_0 , then the total number of molecules adsorbed in the pore will be $N_0 = \theta_0 S/s_0$, where S/s_0 is the number of adsorption sites, obtained as the ratio of the total internal area of a pore and the average area of an adsorption site.

2.1. Coupling with a plug flow model. In a plug flow model, the transport of a species through the reactor is modeled using the following equation:

$$(15) \quad \frac{\partial n}{\partial t} + u \frac{\partial n}{\partial z} = \frac{2}{R}(G - L)$$

where u is the mean flow velocity, G is the surface gain term, L is the surface loss term and R is the reactor radius or the distance between parallel plates in a cross flow reactor.

The loss term is simply the diffusion into the pore:

$$(16) \quad L = f \frac{1}{4} v_{th} n$$

and the gain term is due to out diffusion:

$$(17) \quad G = f \frac{1}{\tau_d} \frac{N}{S_{op}}$$

Here S_{op} is the surface area of the pore opening and f is a factor taking into account the transparency of the MCP and the fractional area of the surface occupied (1/2 in a parallel plate reactor).

From the model above, it is clear that, in equilibrium, the net difference between gain and loss is zero. However, during purging this equilibrium breaks down. We start from $n = 0$ at the entrance of the reactor and this purge pulse propagates downstream. In the meantime, the surface of the pores still contains a fractional coverage θ_0 . This will act as a net source of precursor molecules to the reactor.

2.2. General solution of the model. We need to solve:

$$(18) \quad \frac{\partial n}{\partial t} + u \frac{\partial n}{\partial z} = \frac{2f}{RS_{op}} \left(\frac{1}{\tau_d} N - \frac{1}{4} S_{op} v_{th} n \right)$$

coupled to:

$$(19) \quad \frac{dN}{dt} = \frac{1}{4} S_{op} v_{th} n - \frac{1}{\tau_d} N$$

subject to $N(z, 0) = N_0 = \theta_0 S / s_0$ and $n(0, t) = 0$. τ_d . τ_d can then be obtained from:

$$(20) \quad \tau_d = \left(1 + \theta_0 \frac{4k_B T}{p_0 s_0 d} \right) \tau_{diff}$$

All the coefficients can be derived from the experimental conditions, plus our assumption for the adsorption isotherm by assigning values to θ_0 and p_0 .

Before giving the solution for a situation relevant to the MCP case, it can be shown that it is possible to reduce the problem to:

$$(21) \quad \frac{\partial X}{\partial r} = \frac{\alpha}{1 - e^{-\alpha}} Y - \alpha X$$

and

$$(22) \quad \frac{\partial Y}{\partial s} = (1 - e^{-\alpha}) X - Y$$

where:

$$(23) \quad X = n/n_0$$

$$(24) \quad Y = N/N_0$$

$$(25) \quad r = z/l$$

$$(26) \quad s = \frac{t}{\tau_d} - \frac{z}{u\tau_d}$$

$$(27) \quad n_0 = \frac{8\theta_0}{s_0 v_{th} \tau_d} \frac{L}{d} (1 - e^{-\alpha})$$

$$(28) \quad \alpha = \frac{f v_{th} l}{2Ru}$$

Here l is the size of the substrate, L is the pore depth, and d is the pore diameter. The main reason for bothering in reducing the model into its non-dimensional form is that it identifies α as the main parameter controlling the behavior in the system:

$$(29) \quad n(t, z) = n_0 X((t - z/u)/\tau_d, z/L; \alpha)$$

$$(30) \quad N(t, z) = N_0 Y((t - z/u)/\tau_d, z/L; \alpha)$$

Anything that changes α will have an impact on the desorption of the MCP pores.

Note. *According to the model, the most effective changes in the experimental conditions are those that affect α the most.*

2.3. Application to the MCP case.

2.3.1. *Water and precursor reference cases.* We will define some reasonable conditions as our reference case for both water and precursor purging.

TABLE 1. Main parameters for the reference case

Symbol	Parameter	Value
d	MCP diameter	20 μm
$2L$	MCP width	1.2 mm
$2f$	MCP transparency	0.6
l	MCP substrate size	200 mm
M	Molecular mass (water)	18 amu
M	Molecular mass (precursor)	150 amu
u	mean flow velocity	1 m/s
T	temperature	473 K
s_0	average adsorption site	10 \AA^2
R	characteristic reactor width	2 cm
p_0	dose pressure (water)	100 mTorr
p_0	dose pressure (precursor)	10 mTorr
θ_0	initial physisorption coverage	0.01

In absence of physisorption, the characteristic diffusion time τ_{diff} is 2.2 ms for water and 6.6 ms for the precursor case. By considering a 1% coverage of physisorbed species, the characteristic desorption time τ_d becomes 25 and 660 ms, respectively. Therefore, physisorbed species have the potential of further increasing purge times with respect to the ideal out-diffusion case.

Figures 3 and 4 show the water partial pressure in the gas phase over the MCP and the relative surface coverage for the reference conditions shown in Table 1.

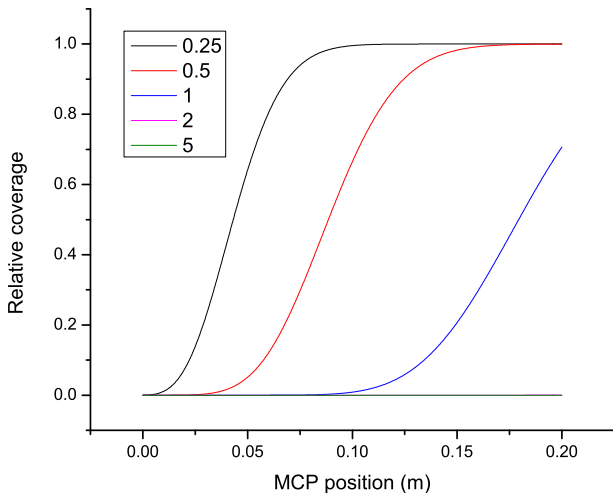


FIGURE 3. Relative physisorbed coverage inside the MCP pores as a function of MCP position for different purge times.

Even after 1s purge the amount of adsorbed water at the end of the MCP has reduced by less than half. Therefore, for the downstream section of the MCP, characteristic desorption times go from being of the millisecond order in absence of physisorption to 25 millisecond for an isolated pore to 1 s when a 20 cm MCP is considered.

The reason for such dramatic increase is clear from Figure 4. At the entrance of the MCP, there is no water partial pressure in the reactor. As the flow moves over the MCP, the partial pressure increases, until reaching an equilibrium with the adsorbed water inside the pores, which delays the out diffusion process downstream. Only when the upstream water is eventually pushed downstream, the downstream pores begin to empty up. As can be seen from Figs. 3 and 4, this effect is strongly size-dependent: if only 2 cm piece is considered, the outgassing takes place in less than half a second.

We can see the effect of MCP position on desorption by following the coverage as a function of time for different positions in the MCP. Figure 5 follows five points located at 0, 5, 10, 15 and 20 cm from the upstream position.

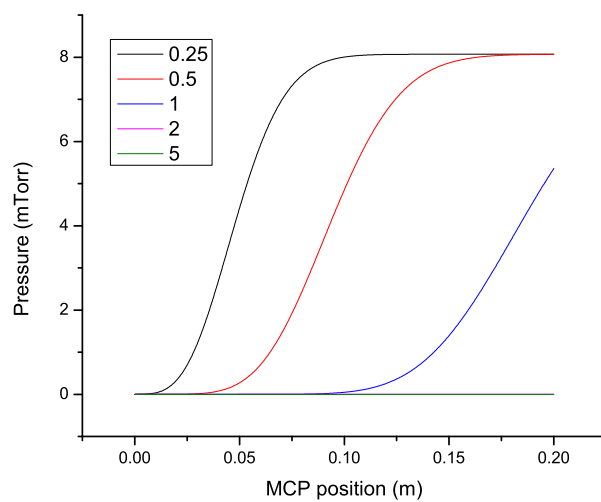


FIGURE 4. Water partial pressure above the MCP as a function of MCP position for different purge times.

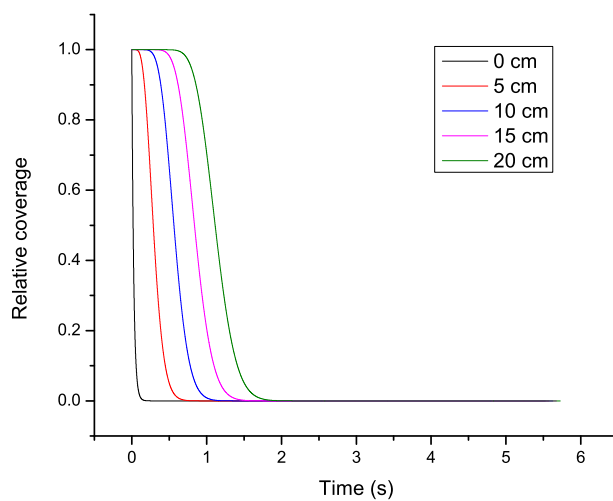


FIGURE 5. Change with time of relative coverage at different positions in an MCP substrate

The situation is even worse in the precursor reference case. As shown in Figs. 6 and 7, after 5 seconds of purging the concentration of physisorbed precursors in the pores on the downstream half of the MCP has barely started to go down.

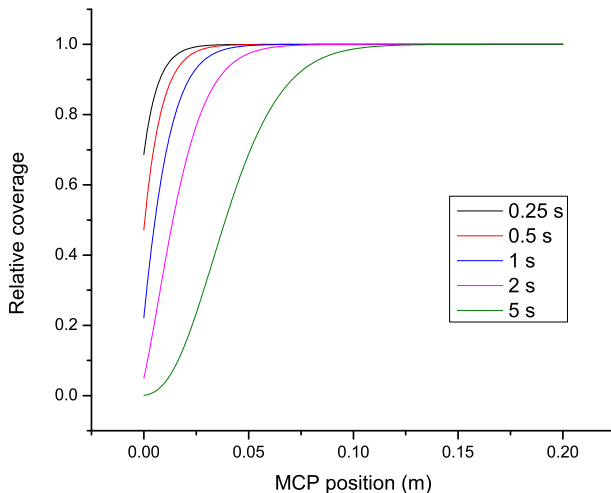


FIGURE 6. Relative physisorbed coverage of precursor inside the MCP pores as a function of MCP position for different purge times.

As in the water case, the characteristic time for out-diffusion that can be estimated from the time profiles at different positions on the MCP (Figure 8) is much longer than the estimated 600 ms for the isolated pores.

The significantly worse performance of the precursor compared to water comes mainly from two factors: the larger mass, which slows down the out diffusion process, and the lower partial pressure used in the reference case (precursors are more sticky).

As shown in the previous section, much of the physics is contained in the parameter α :

$$(31) \quad \alpha = \frac{fv_{th}l}{2Ru}$$

Lower values of α tend to mitigate the problem in the downstream section of the MCP: larger cross sections or top-bottom distances (R) in the reactor, larger velocities v or a reduction of the density of pores (not viable for the MCP case) tend to give more homogeneous profiles. As it is also apparent from the definition of α and the results shown above, the problem is compounded for large substrates (large l).

The dependence of the substrate size emphasizes the fact that the increase in desorption times is a consequence of a cascade effect. It can be shown that the surface coverage

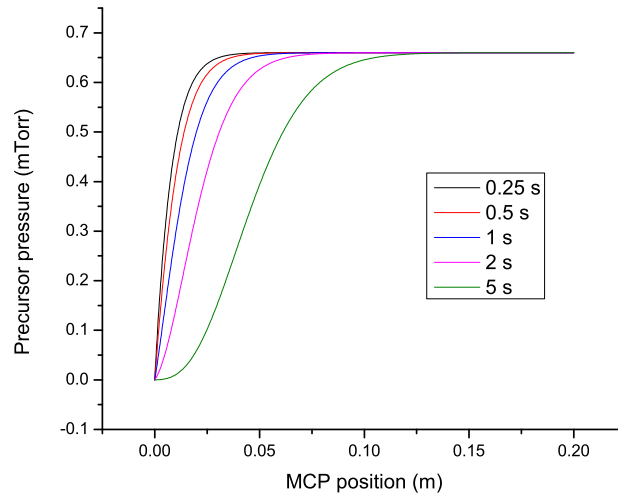


FIGURE 7. Precursor partial pressure above the MCP as a function of MCP position for different purge times.

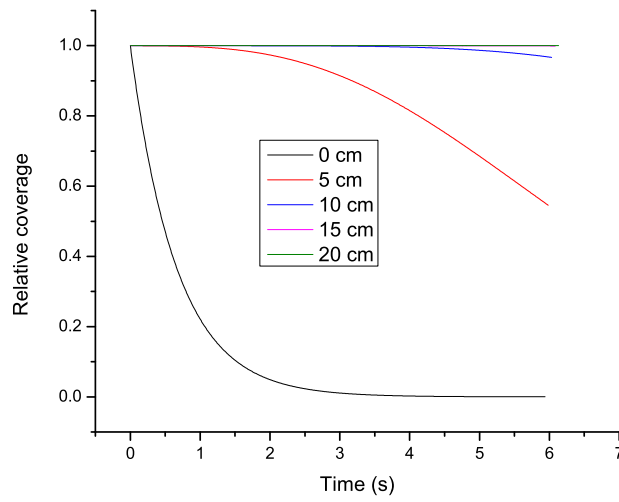


FIGURE 8. Change with time of relative precursor coverage at different positions in an MCP substrate

depends on the previous history of the precursor partial pressure at that particular point:

$$(32) \quad \theta(t, z) = \theta_0 e^{-(t-z/u)/\tau_d} + c \int_0^{t-z/u} dt' n(z, t') e^{t'/\tau_d} e^{-(t-z/u)/\tau_d}$$

Where c is a constant that depends on the experimental conditions. Smaller substrates lead to lower partial pressures and to a smaller effect of readsorption on desorption times.

2.4. Model limitations. This is the simplest possible model that captures the complexities of purging large area nanoporous substrates. A more accurate representation would solve the transport equation in each section of the MCP. Also, we have neglected axial diffusion, which can lead to back-diffusion in the cases where large gradients in precursor pressure are present across the MCP. Finally, a 2D picture would provide a better understanding of the precursor dynamics over the MCP area, including any stagnation generated by precursor gradients opposing the direction of flow due to precursor build-up on the downstream area of the MCP plates.

Note. *Caveat emptor: we don't have any experimental evidence on the presence of these physisorbed species. We might be focusing on something that may not exist.*