Theoretical and experimental molecular beam angular distribution studies for gas injection in ultra-high vacuum

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Abstract

A dedicated set-up was designed and constructed for the purpose of accurately measuring flux distributions out of gas injectors of various shapes into ultra-high vacuum (UHV). Angular flux profiles of nitrogen exiting through various axially symmetric injectors over a range of flow rates are measured. The intent of these experiments is to validate a self-consistent simulation model based on the cosine law of molecular scattering on the walls. The experimental results give a clear confirmation of the proposed model within the limits of the molecular flow regime. Beyond this limit, the experimental profiles become flow rate dependent and gradually deviate from the model predictions.

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1. Introduction

In order to maximize fabrication yield, device manufacturers require thin films with extremely uniform thickness, composition and doping level on large substrates (≥ 100 mm diameter). Currently, most deposition systems take advantage of the averaging effects of substrate rotation, combined with diffuse injection of the source species in order to achieve the high uniformity (better than 1%) necessary to comply with these requirements. These performances are obtained at the expense of source-use efficiency (usually below 10%) resulting in most of the injected species missing the growth surface and being either pumped out or collected by the cryopanels. Considering the high cost per gram of the chemical sources involved, more efficient gas injectors would generate significant savings. However, such an improvement must be achieved without sacrificing the current uniformity levels. Gas injectors optimized for both flux uniformity and efficiency could also eliminate the necessity for substrate rotation which requires the use of mechanically complex and expensive rotating substrate manipulators and can be detrimental to in-situ real-time analysis techniques or even to the growth quality [1,2]. Surprisingly, very little research has been done to systematically optimize the injection of source chemicals in UHV epitaxy systems, especially for gas sources. In order to be able to design optimized injectors for stationary substrates, a fast numerical model simulating accurately the flux distribution of gas emitted from injectors with arbitrary geometry into UHV is needed. Besides, on a more fundamental point of view, such a model would be very useful in understanding transport and injection of highly rarefied gases. Before being used as a tool for injector design, the model needs to be validated by comparing its results with carefully controlled experimental data.

Similar studies have been carried out by other groups either for elemental sources molecular beam epitaxy (ESMBE) [3–6] or for other deposition techniques [7]. Typically, model validation was achieved by fitting simulation data to measured thickness profiles on grown layers using several adjustable parameters. In this work, gaseous sources were used and validation was obtained using a set-up specially designed for flux distribution measurements and a variety of conical and cylindrical injectors.

The aim of this work was to explore the domain of validity of a simple and general model based on the cosine law of molecular scattering on the walls for calculating gas flux distribution. This was done using a dedicated test bench designed to directly measure gas flux distributions. In order to insure the generality of the model, the number of adjustable parameters was reduced to a minimum. Once its domain of validity is established, the model will be used to simulate complex injectors and optimize their geometry.

2. Model description

The mathematical background behind the model used in this work was originally proposed by Wu [8] as a discrete solution to a
collisionless Boltzmann equation. Models based on the same calculation technique have been previously used by other research groups [3,4]. The one described in the paper is based on the following physical hypotheses:

1. Emission from the injector’s inlet (source) is uniform and assumes a cosine distribution,
2. Molecules are diffusively scattered on the walls with negligible sorption, backscattering, specular reflection or surface diffusion implying that all the molecules impinging on an area are instantaneously re-emitted from the same location in a cosine angular distribution,
3. Molecules travel in straight line between two wall collisions implying no long range interactions (billiard-ball type of motion) and a mean free path much longer than the characteristic geometrical dimensions (both inside the injector and the chamber),
4. Contributions from the molecules that are scattered from the chamber back into the injector are negligible (very high vacuum maintained inside the chamber),
5. The gas temperature is determined by the wall temperature and is assumed to be isothermal,
6. Steady-state flow prevails (no parameter is time-dependent).

If needed, some of these assumptions may be relaxed at the expense of code simplicity and speed of processing.

The model is based on the flux exchange equation between two differential area assuming cosine emission and the line of sight flux [9]. The flux \( dF \) exchanged between area elements \( dS_1 \) (source) and \( dS_2 \) (target) is given by

\[
dF = (I_1 dS_1 \cos \theta_1 d\Omega_1 - I_2 dS_2 \cos \theta_2 d\Omega_2)/\pi,
\]

where \( d\Omega_1 \) is the solid angle subtended by \( dS_2 \) from \( dS_1 \) given by

\[
d\Omega_2 = (dS_2 \cos \theta_2)/D^2,
\]

where \( D \) is the total flux density emitted by \( dS_1 \) and \( dS_2 \) are the angles between the line, of length \( D \), joining the centers of the two elements, \( dS_1 \) and \( dS_2 \) and their respective normal vectors (Fig. 1).

Simulations are carried out using a three-steps process described below:

1. 2D-meshing of all the surfaces involved (injector and target),
2. Calculations of the flux exchanged inside the injector,
3. Calculations of the flux received by the target from the injector.

The assumption that a negligible quantity of molecules are scattered back inside the injector, from the surrounding vacuum, allows the calculations of the last two steps to be carried out separately, effectively neglecting any contribution from the exterior of the injector.

In step 1, all the walls inside the injector as well as those of the target are divided in small area elements each of them being associated with its center point.

During step 2, iterative calculations of the flux exchanged between all the elements of the injector are carried out self-consistently using Eq. (1). This results in the steady-state flux densities impinging on each area element. These calculations are based on the fact that molecules impinging on one element are originating from all the other parts of the injector and may be divided into those coming directly from the source and those having previously undergone a certain number of collisions on the walls. Thus, the total flux impinging on one element is given by the summation of the contributions from all the other elements for molecules having undergone zero to an infinite number of collisions. Considering the fact that some of molecules exit the injector after each new collision, the magnitude of the summation terms will quickly decrease with the number of collisions, insuring the convergence of the summation and facilitating its computation. The higher summation terms are, therefore, very small and the summation can be stopped when the remainder becomes negligible compared to the ongoing sum total.

Step 3 consists in calculating the flux going from each element of the injector to each discrete area element on the target. The target geometry and position may be chosen arbitrarily. For instance, for gas impinging on a wafer, it is set as a disk. Again, Eq. (1) is used, but this time, an extra test must be added to exclude exchanges between surface elements that have no direct line of sight, the so-called “shadowing effects”. For diverging conical nozzles (including cylinders) studied here, this test simply consists in calculating the coordinates of the points where the straight line between two elements intersects an infinite cone and then testing if it lies on the real nozzle. For more complex geometries, a more general procedure is needed.

For the purpose of validating the physical model, the preliminary version of the code was limited to basic axially symmetric injectors (divergent cones, cylinders and thin orifices) containing no baffles. However, the model is completely general and by no means limited to any specific geometry. Complex injector geometries require a more extensive code, which is slower to run, more demanding on computer memory and much more difficult to validate. In the cases involving baffles or non-convex shapes, shadowing effects inside the injector need to be taken into account in step 2.

All the calculations are carried out using matrices in a MATLAB environment which results in short computation times (typically 2–30 s for a complete flux map depending on the geometry, accuracy and spatial resolution needed). Speed of calculation is a strong point of this model which compares advantageously to the commonly used Monte Carlo method. Its other advantages include self-consistency, simplicity, generality (it is not limited to a specific geometry) and its possible extension beyond its basic assumptions. Accuracy of the results can be improved using a more aggressive mesh (smaller element areas) at the expense of calculation time and computer memory. The model being linear, extending its application to multi-nozzle injectors only requires the superposition of each nozzle’s flux profile according to its spatial position.
As a first-order validation, results from the model can be compared with acknowledged data from the literature. The transmission probability of a vacuum component, also referred to as its Clausing factor (CF) [10] is defined as the probability, for a molecule entering it according to the cosine law, of exiting through the opposite end. Variational methods have been used by Cole [11] to calculate the upper and lower bounds to the transmission probability for tubes whose ratio of length to radius $(L/R)$ ranged from 0.1 to 1000. His results are often cited as the most precise and reliable data and they correlate very well with those of Nawyn and Meyer [12]. Using the model previously described, there are two methods for calculating the CF of an injector. The first one (Method1) uses only step 2 intermediate results to get the normalized flow exiting the injector. The other one (Method2) consists in summing the fluxes impinging on a half-sphere centered on the injector inlet, thus using both steps 2 and 3. Table 1 compares CF values given by Cole for tubes of various $L/R$ with results obtained using the methods previously described. The relative error is of the order or below 1% for all $L/R$ except the largest one. All the calculations have been done using the same number of discrete elements for the injector walls. As mentioned earlier, the number of elements can be increased in order to improve the results’ accuracy. The very good agreement with Cole’s data is a proof of the validity of the code written for steps 2 and 3 (at least for tubes).

Strictly speaking, Eqs. (1) and (2) are only valid for elements of infinite small area. The approximate results they give are fairly good as long as $dS_1$ and $dS_2$ are small compared to $D^2$. In principle, as the element areas become smaller, the results should become more accurate [8]. However, this is not true for elements between the very edge of the inlet disc and the closest edge of the conical surface. At these corners, $D^2$ scales as fast as $dS$ resulting in a systematic error in Eq. (1) which propagates to the entire calculations. One way out of this problem is to use an integral version of Eq. (1) over one or both surfaces. Due to the similarity between the propagation laws of radiations and of free molecules, similar integrals have already been evaluated by researchers in radiative heat transfer. They are listed in a catalog [13] as radiation configuration factors or “view factors” (VF) which are given by the following general formula:

$$\text{(VF)}_{12} = \frac{1}{S_1} \int_{S_1} \int_{S_2} (\cos \theta_1 \cos \theta_2 dS_1 dS_2) \frac{1}{\pi D^2}.$$  

The flux between two finite areas $S_1$ and $S_2$ is then given by $I_1 S_1 (\text{VF})_{12}$ if the flux density emitted by $S_1$ is assumed to be uniform across the emission area. Because this hypothesis is the only approximation used, the Clausing factors derived using VF are much more accurate than the previous ones using Eq. (1). The superiority of this method is clearly shown in Table 1 as its calculated CF values are essentially identical to Cole’s results.

### Table 1
Comparison between Clausing factors for tubes calculated by Cole and with the present model (using either view factors or discrete area elements).

<table>
<thead>
<tr>
<th>$L/R$</th>
<th>Cole’s data</th>
<th>View factors</th>
<th>Discrete area elements</th>
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<td></td>
<td>Method1 Error (%)</td>
<td>Method2 Error (%)</td>
<td></td>
</tr>
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<td>0.952399 0.9528</td>
<td>0.04</td>
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<tr>
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<td>0.671984 0.6714</td>
<td>−0.1</td>
</tr>
<tr>
<td>2</td>
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<td>0.514231 0.5106</td>
<td>−0.7</td>
</tr>
<tr>
<td>3</td>
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<td>10</td>
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<td>20</td>
<td>0.10930</td>
<td>0.10926 0.0944</td>
<td>−14</td>
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### 3. Experimental

In order to experimentally validate the model, the dedicated set-up shown in Fig. 2 has been designed and built. It consists in a 911 UHV chamber equipped with a 8801/s (69,500 Torr sccm) turbo-pump with a base pressure around $7 \times 10^{-8}$ Torr. This pumping capacity is sufficient to maintain the chamber at a pressure below $3 \times 10^{-5}$ Torr for flow rates as high as 1.5 sccm. The injection tube is introduced through the top of the chamber. Vertical and rotational motion is made possible by stepper motors and multi-axes motion feedthroughs. An encapsulated Bayard–Alpert gauge (BAG) was chosen as sensor because of its high sensitivity to very small fluxes. The gauge enclosure has an opening with an area that is much smaller than the enclosure internal surface, insuring a complete randomization of molecular directions inside it and thus avoiding any “beaming effect” [14]. Once a steady-state pressure is reached inside the box, the net flow crossing its orifice is zero as the incoming flow ($F_{in}$) from the injector and the chamber walls balances the outgoing flow ($F_{out}$) from the box. With the gas motion inside the chamber and the box assumed isotropic, the outgoing flow is proportional to the total pressure inside the box. Since $F_{in}=F_{out}$ the total pressure in the can is therefore proportional to the incoming flow. The gas entering the box from the chamber walls as well as other small effects (transpiration and outgassing from the box) give a constant contribution (independent of the box position) which only adds an offset to this linear relationship. This offset or background flux density can be measured independently simply by injecting the gas away from the line of sight of the orifice (VENT line). Encapsulating the gauge strongly decreases the background signal from molecules re-emitted by the surrounding chamber walls.
since they can only enter the box through a very small hole. Similar flux sensors have previously been used by other groups and have shown excellent sensitivity [14,15]. The encapsulated BAG is attached to a rocking pendulum assembly that keeps the sensor aligned with the center of the injector inlet at all times. The angle of the pendulum is varied using a stepper motor driven actuator that is attached to the pendulum arm. It can be controlled with an accuracy better than 0.1° via a LabView™ software. A second BAG is located on the side of the chamber. The pendulum motion of the flux-sensing gauge allows for the generation of angular gas flow profiles.

Several injectors were machined from stainless steel with ‘mirror polished’ finish (macroscopically smooth at the micron level). A quick mounting system allows for easy injector change. Right before the injector inlet, a randomizer, consisting of several sheets of thin paper, is inserted in order to comply with the model’s assumption of uniform and diffuse emission at the source. Since molecules have to permeate through it, its effect is to insure that the inlet flux distribution does not vary with the upstream conditions. The flow rate through the injector is precisely controlled via a pressure cell consisting in a volume bounded by an adjustable valve at the entrance and a small orifice at the exit. The valve opening is controlled to maintain a constant pressure within the cell, as measured by a capacitance manometer. This technique is widely used in gas source UHV epitaxy tools and exhibits unmatched flux reproducibility and stability. The flow rate passing through the injector can be read on a thermal mass flow meter (MFM) situated upstream of the pressure cell. A second gas line allows for redirection of the gas flow away from the injection tube, towards a second port through the side of the chamber (VENT line). It is fitted with a manual needle valve that is adjusted to match the conductance of the line going through injector (RUN line). A double valve cell is used to switch the flow either to the RUN or to the VENT line. As will be discussed later, the purpose of the VENT line is to provide an independent measurement of the background level inside the sensor. For all the results presented here, the test gas is pre-purified nitrogen, the injectors have an inlet diameter of 1.9 ± 0.1 mm and a maximum length of 20.1 mm, the distance between the nozzle’s and the sensor’s inlets is 51 ± 0.5 mm and the box orifice has a diameter of 2.1 ± 0.1 mm.

Before each individual injector characterization, the pressure signals from both BAGs were measured against the flow rate as given by the MFM. This systematically resulted in very linear curves at least up to pressures around 1 × 10⁻⁴ Torr as shown in Fig. 3 and in agreement with the results of Adamson [14]. This allows the fixed gauge to be used as flow rate measurement device even at very low flows where the MFM readings become unreliable. For the mobile gauge, it is a basic linearity check that cannot be used any further since the slope of the line depends on the gauge position. During profile measurements, at each polar angle, the encapsulated gauge signal is given sufficient time to stabilize, allowing the pressure inside the enclosure to reach a steady state. The electronic noise in the gauge signal is filtered out by time averaging. The pressure readings of both the mobile and fixed gauges are collected, the latter data being used only to insure that the chamber is kept in the molecular flow regime and to monitor the effect of the mobile gauge position on the chamber pressure.

The characterization of an injector consists in acquiring flux data along an arc (arc-scan) at various flow rates. Once the desired flow rate is stabilized, an arc-scan of typically 64 points in both directions is acquired using the RUN line (signal+background). The flow is then switched to the VENT line and after its conductance is adjusted to match the RUN line (same pressure reading on the fixed BAG), a short scan is acquired in order to get the average background pressure inside the box. This data is used later during the curve fitting. For each injector, scans are acquired for a range of flow rates starting at the lowest controllable flow and increasing it by a factor of about two each time.

4. Results and discussion

The fitting process consists in generating a flux simulation on the arc corresponding to the measurements, adjusting its peak position, adding the measured background level and finally adjusting its height using a scaling factor in order to obtain the best fit of the experimental data. Thus, the only adjustable parameters are the scaling factor and the centerline position (origin of the angles).

In the case of a thin orifice, the model fits the experimental data very closely and can be superimposed to a cosine function (Fig. 4), as predicted by theory. This proves the validity of the cosine law at the injector inlet and thus the adequate performance.
of the randomizer as an effusion source. As a more generic form of injectors, a frustum of a cone was tested using low (0.07 sccm) and high (1.2 sccm) flow rates. The data and simulation are given in Fig. 5. The quality of the fit between data and simulation is excellent for the low flow rate, but a significant deterioration is observed as the flow rate is increased, because of the effects of intermolecular collisions within the injector. In these conditions, the model breaks down since one of the hypotheses on which it relies is not fulfilled any more. However, in the low flow regime, the excellent agreement between the simulated and experimental data is proof of the validity of the model. Another way to verify the model’s performance is through simple geometry. Assuming that the flux density emitted by the inlet disk (source) is much larger than that of the injector walls, one can identify three zones in the angular flux profile of a given injector. Zone 1 includes all angles where the inlet disk is not shadowed by the injector walls. It is characterized by a modified cosine angular dependence. In zone 2, the flux intensity drops abruptly, as the inlet disk is progressively shadowed by the injector walls. Finally, in zone 3, molecules reaching the target are emitted solely by the injector walls and produce a slowly decreasing tail. The limits of the different zones can be calculated from the injector geometry and are identified on Fig. 5. The good agreement between the model, the data and the limits of zone 1 is especially easy to verify. The flat top and the sloped flanks of cylindrical injectors are also well fitted at low flow rates. Being able to fit both the experimental peak height and width using simulation data and only one adjustable parameter is very unlikely unless the simulated curve has the right height to width ratio. Thus the nearly perfect fits obtained for 10° and 15° half-angle cones at low flow rates provides the most convincing proof of the model validity.

As mentioned in Section 3, these measurements are based on the box pressure varying linearly with the injector flux density through the orifice with the flux density from the chamber walls adding a constant offset pressure:

\[ P_{\text{BAG}}(\theta) = \alpha [F_{\text{inj}}(\theta) + F_{\text{walls}}] \]  

where \( P_{\text{BAG}} \) represents the gauge pressure and \( F_{\text{inj}}, F_{\text{walls}} \) the flux density coming, respectively, from the injector and the walls while \( \alpha \) is a constant that relates the BAG pressure with the flux density out of it. If the mobile pressure gauge was perfectly calibrated and its temperature known, \( \alpha \) could be calculated, but this is not necessary if one is only interested in reproducing the shape of the flux profile.

Now the model, being purely geometric and dimensionless, predicts a linear scaling of the flux density (or box pressure) profile with the flow rate. To perform a fit, a simulated profile is generated using an arbitrary flow rate of 1, then the measured background pressure is subtracted from the experimental data and finally the peak height is adjusted using a scaling factor. Therefore, within the domain of validity of the model, one expects the experimental profiles to keep the same shape and the scaling factor to vary linearly with flow rate. This is indeed observed at low flow rates where the model’s assumptions are still valid. As shown in Fig. 6, the fitted scaling factor (as well as the measured background level) for a single injector vary linearly with flow rate up to high values, indicating that once this factor is set for a given flow rate, its value can be calculated for any flow rates inside the molecular flow regime. Fig. 6 also shows that this factor is nearly independent of the injector geometry at low flow rates, limiting the dependency of the fitting parameter solely to flow rate.

For high flow rates, fit quality is degraded and significant widening of the experimental distributions is observed. This can be explained by a change in the flow conditions inside the injector towards the so-called “transition flow regime”. A method to estimate the flow regime using the injector geometry and the flow rate was devised.

The injector transmission probability \( K \) being known, its conductance \( C \) can be deduced using

\[ C = K \nu_s A/4, \]  

where \( \nu_s \) and \( A \) are, respectively, the gas mean molecular velocity and the injector inlet area. Assuming negligible pressure in the chamber just outside the injector, the inlet pressure \( P_i \) can be obtained from \( C \) and the molar flow rate. The mean free path at the source \( (\lambda_s) \) is then given by

\[ \lambda_s = C/(\sqrt{2} \pi d_0^2 N_A F_m), \]  

where \( d_0, N_A \) and \( F_m \) are, respectively, the molecular diameter, Avogadro’s number and the molar flow rate. The ratio of \( \lambda_s \) to the injector’s inlet diameter gives the Knudsen number at the source \( (Kn) \) which can be used to characterize the flow regime inside the

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**Fig. 5.** Angular flux distributions exiting from a conical injector (half-angle 10°) for low (Kn=5) and high (Kn=0.3) flow rates. Left insert shows injector’s details. Right insert shows the injector’s three geometric zones.

**Fig. 6.** Measured background and fitted scaling factor variations with flow rate for three different injectors showing linear scaling nearly independent of the injector’s geometry. Dashed lines are linear fits of the data.
The molecular flow regime is usually defined as the region where $Kn \geq 1$ while the transition flow regime as the one where $1 \geq Kn \geq 0.01$. As shown in Fig. 5, the fit quality for a conical injector is significantly degraded for a value of $Kn$ of 0.3. As the flow rate through the injector is increased, a gradual widening of the angular flux distribution is observed for $Kn$ values below $\approx 1$. This is attributed to the increasing number of intermolecular collisions inside the injector. These collisions reduce the direct flux out of the injector which decreases the peak height while promoting a higher angle exit which increases its width. This widening of flux distributions as $Kn$ decreases towards the transition regime has previously been observed by Stickney et al. [16]. Below $Kn \approx 1$, the proposed model, which assumes a linear dependency of the experimental fluxes with flow rate, starts to break down as the flux distribution becomes flow rate dependent. Modifications of the model in order to include the effects of intermolecular collisions are then needed to accurately simulate the data.

5. Conclusions

A dedicated set-up was used to evaluate a simple and general model for the simulation of gas flux distributions exiting axially symmetric injectors into UHV. Using nitrogen as a test gas, the model predictions show excellent agreement with the experimental data within the limits of its physical assumptions (molecular flow). As the molecules' mean free path decreases below the injector's inlet diameter, intermolecular collisions gradually widen the experimental distributions and this simple model breaks down. Improving the model in order to fit these data would require an upgrade that would take into account molecular interactions within the volume of the injector. The present work has shown that gas flux distributions out of a gas injector are flow rate independent only within the molecular flow regime. If a stationary substrate is to be used for thin film deposition using molecular beams, it will be necessary to carefully choose the injector's dimensions in order to insure molecular flow over the range of useful flow rates. For example, the growth of GaAs by CBE at 1 $\mu$m/hr on a 100 mm diameter wafer, assuming a source efficiency of 10%, requires a flow rate of $\approx 1.1$ sccm of trimethylgallium (TMG). In order to reach a $Kn$ value of 5, assuming a molecular diameter of 6 Å for TMG and a short injector (CF of 0.8), a 6 cm inlet diameter is required. This is quite unrealistic and the model applicability seems to be compromised for the design of single injectors for CBE. However, the model being linear, if molecular flow prevails inside the chamber, the superposition principle can be used to simulate multi-nozzle injection devices. In that case, with each nozzle injecting only a fraction of the total flow rate, the restrictions on their dimensions are much less stringent. Then the predicting capabilities of the present model can be used to design optimized CBE injectors capable of insuring high levels of both flux uniformity and source use efficiency for rotating or stationary substrates.

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