

Zinc Deposition Experiments for Validation of DSMC Calculations of Internal Flows

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Abstract. Experiments specially designed for this purpose have been performed for the validation of DSMC calculations of internal flows. Hot zinc vapor is released into a cold wall deposition chamber in which two silicon wafers are mounted. The deposited zinc layers on these wafers have been measured in four different experiments, with varying background gas species (argon and helium) and background pressures. The experimental results have been compared to simulation results. The background gas conditions are chosen such that the Knudsen numbers based on the zinc mean free path range from 0.34 to 2.8.

INTRODUCTION

A multi-purpose, 3D, curvilinear mesh DSMC code [1, 2] based on the method as described by Bird [3] is being developed in collaboration between Delft University of Technology and the Netherlands Organisation for Applied Scientific Research TNO for calculating internal rarefied gas flows with chemical reactions. One of the main application area's for this code is the field of Chemical Vapor Deposition (CVD) [4]. The code has been validated using a wide range of literature results, but no usefull experimental data was found in the field of deposition of thin films. The main reason for this is the fact that most experiments are aimed at creating perfectly uniform films, *e.g.* [5], which is not ideal from the validation point of view. Also, existing literature usually does not provide precise information of the conditions, *e.g.* temperature and pressure. Therefore, an experiment was designed in which the conditions could be monitored and controlled with sufficient accuracy, and, more importantly, in which the deposited films were not uniform. The goal of the experiment was to deposit a thin metal film on a surface, and to compare thickness measurements of this film to DSMC calculations.

EXPERIMENTAL SETUP

The experiments were performed in a large ($\sim 1 \text{ m}^3$) vacuum vessel which could be evacuated down to around 10^{-5} Pa . An accurately known argon or helium background pressure could be introduced in the vessel. Inside the large vessel, a smaller ($\sim 1.5 \cdot 10^{-3} \text{ m}^3$) cold wall deposition chamber was used for the actual experiment. The deposition chamber (see figure 1) was connected to the vessel through a large 4 cm hole at the top. An effusion source filled with liquid zinc was mounted at the bottom of the chamber. This source provided a steady flux of hot zinc vapor into the chamber, where the zinc would deposit on the cold walls. To facilitate measurements on the deposited layers, silicon wafers were mounted inside the chamber. The wafers could be removed from the setup to be subjected to zinc layer thickness measurements.

An experimental run consisted of the following steps:

- placement of new wafers inside the chamber
- evacuation of the vacuum vessel to at least $2 \cdot 10^{-4} \text{ Pa}$ (measured on a separate Bayard-Alpert ion gauge), which is a factor 100 lower than the lowest operating pressure
- heating of the source and the zinc to the required temperature (± 25 minutes)
- introduction of the background gas, setting the pressure and waiting for stabilization (± 5 minutes)
- opening and closing of the shutter, that separates the zinc source from the deposition chamber (300 seconds open time)

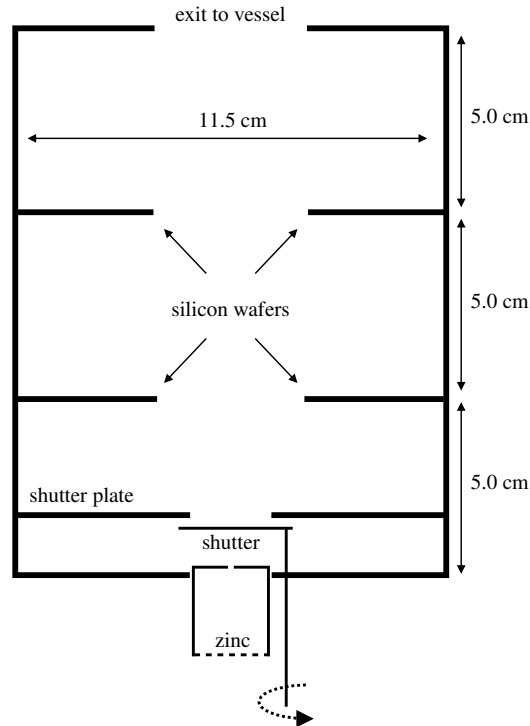


FIGURE 1. The geometry of the deposition chamber. The wafer closest to the zinc source will be referred to as the bottom wafer, the other one as the top wafer. Note that only the shutter can be rotated, the shutter plate is fixed.

- closing the background gas supply
- cooling of the zinc (it took ± 7 minutes before the zinc solidified again)
- (after cooling to below 100°C) aeration of the vessel
- measurements of the zinc layer thickness

An arrangement of a shutter and shutter plate was needed to be able to accurately determine the deposition time. In the closed position, the combination of the shutter and the shutter plate could completely separate the top of the chamber from the source. This was necessary to prevent zinc from depositing on the wafers during the heating and cooling of the zinc. It was checked experimentally that no zinc reached the wafers with the shutter closed.

See figure 1 for a schematic overview of all components. Please note that the geometry is axi-symmetric. The wafers used for the experiment were prepared with a 4 cm hole in the center to let the zinc flow past both wafers and to allow the background gas to reach the orifice easily. The inner diameter of the chamber is 11.5 cm, and the height of the three sections is 5.0 cm. The vertical distance between the orifice and the bottom wafer is 4.75 cm. The shutter plate is fixed 1.6 cm above the chamber bottom and has a 2 cm \varnothing hole.

Background gas conditions

Three of the four experiments were performed using argon as a background gas at three different pressures: 0.031, 0.088 and 0.25 Pa. The mean free path of zinc atoms at room temperature in these situations is 14, 5.0 and 1.7 cm, respectively. This gives Knudsen numbers (based on the distance between the two wafers) of 2.8, 1.0 and 0.34. The last experiment was done using helium at 0.088 Pa. The mean free path of zinc is 3.0 cm at this pressure, resulting in a Knudsen number of 0.60. The background pressure could be obtained and kept steady using a needle valve gas inlet in combination with a throttle on the diffusion pump. Accurate measurements were done in the large vacuum vessel using a Pfeiffer CMR 275 Capacitance Gauge, with an error of less than 1% of the measured value.

The main influence of the background conditions on the deposition profile can be seen on the top wafer. When the pressure is low, zinc atoms travel from the orifice to the wafers (almost) without collisions. The resulting deposition profile on the top wafer will then have a sharp transition due to the shadow effect of the bottom wafer. At high pressures, the zinc atoms collide a few times before reaching the top wafer, and thus the shadow effect will be much less and the transition much smoother.

Temperature control

The commercial effusion source (NTEZ40 from MBE) contained two type K thermocouples and a hot filament to heat the contents. The temperature was controlled using a PID controller and one of the two available thermocouples. The zinc in the source was kept at a steady temperature of 718 K, which is just above the melting temperature of 692.7 K. The reading of the thermocouple differed from the actual zinc temperature, and calibration was done using a thermocouple inside the zinc. The difference between the reading and the zinc temperature was approximately 35 K. The calibration also provided data about the time it took for the zinc temperature to reach the steady state. The source was separated from the chamber by a small 2 mm Ø orifice which was 0.2 mm thick. The temperature of the orifice was actively monitored using a thin type K thermocouple, and maintained at a value of 700 K by a PID controlled resistance heater soldered onto the orifice. This was necessary to prevent formation of a solid zinc film on the orifice which could eventually block the hole. The temperature of the walls of the deposition chamber was measured during all experimental runs using a standard type K thermocouple. Due to the large thermal mass of the chamber, the temperature did not significantly vary from the room temperature of 292 K. The temperature of the bottom wafer was also monitored using a thermocouple. Its temperature increased slightly during an experimental run due to the radiation from the heated orifice, but the temperature rise never exceeded 8 K.

Surface treatment

Before each experimental run, the wafers were cleaned extensively in a nitrogen and an oxygen plasma barrel etcher run. It was found that the sticking coefficient on the silicon itself (even after extensive cleaning) was very low, and therefore the lower sides of the wafers (*i.e.* the sides facing the zinc source) were coated with a thin (50 nm) molybdenum layer to improve sticking of the zinc. The top sides were not coated. As a result, very little zinc deposited on these sides. Also, little zinc was found to deposit on all other walls in the deposition chamber.

After an experimental run, the wafers were processed as quickly as possible to reduce the influence of the formation of an oxide layer. The zinc layer was removed along two thin (~ 1 mm) lines, extending radially from the center to the edge of the wafer, and the thickness of the zinc was measured at several locations. These measurements were performed using a Veeco Dektak 8 surface profiler with a 5 μm tip and a force of 4 mg. The inaccuracy is approximately 5 nm.

The zinc removal was done by HCl etching. The path to be etched was first surrounded by polyamide tape. Then, diluted HCl was applied to the exposed zinc and washed away with purified water after approximately 30 seconds. The tape was then removed and the wafer dried using clean N_2 gas. Zinc is quickly dissolved in the HCl solution, while the molybdenum layer is not affected. No zinc was found on the tape after removal.

NUMERICAL SETUP

The DSMC computations were performed using a parallelised multi-block code, with a 2D axi-symmetric computational domain that included the entire deposition chamber. The incoming zinc flux at the orifice was modelled using a massflow boundary condition. The flux of zinc atoms through the orifice can be calculated using the zinc vapor pressure p_v in mm of mercury [6, p. D-215]:

$$\log_{10} p_v = -\frac{0.05223 \cdot 118000}{T} + 8.108 \quad (1)$$

The temperature T is in Kelvin, and is taken to be the lowest temperature in the system surrounding the liquid zinc, in this case the temperature of the orifice (700 K). The flux is calculated as $\frac{1}{4}n_v c$, with vapor number density $n_v = 2.77 \cdot 10^{21} \text{ m}^{-3}$ calculated from equation (1) and thermal velocity c . The computational particles are introduced in

TABLE 1. Species parameters for VSS collision model.

	Zinc	Argon	Helium
mass (kg)	$108.6 \cdot 10^{-27}$	$66.3 \cdot 10^{-27}$	$6.65 \cdot 10^{-27}$
reference diameter (m)	$4.05 \cdot 10^{-10}$	$3.50 \cdot 10^{-10}$	$2.13 \cdot 10^{-10}$
reference temperature (K)	700	700	700
viscosity temperature exponent	0.88	0.74	0.64
VSS parameter α	1.68	1.50	1.21

TABLE 2. DSMC calculation settings.

	Argon	Argon	Argon	Helium
pressure	0.031 Pa	0.088 Pa	0.25 Pa	0.088 Pa
Δt (s)	$5.0 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$
F_{num}	$1.0 \cdot 10^{11}$	$3.0 \cdot 10^{10}$	$8.0 \cdot 10^9$	$3.0 \cdot 10^{10}$
cell size far from orifice (m)	$5.0 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
cell size near orifice (m)	$4.75 \cdot 10^{-3}$	$1.85 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	$1.85 \cdot 10^{-3}$

the domain with a velocity sampled from a Maxwellian with zero average. To enforce the massflux, no computational particles were allowed to leave the computational domain through the orifice. If a particle crossed this surface, it was subjected to a diffuse reflection. At the top of the chamber, a stream boundary condition was used, with properties of the background gas in the large vessel.

The sticking coefficient of zinc atoms on the bottom sides of the wafers (which were coated with molybdenum) was estimated to be 0.9. The sticking coefficient on all other cold surfaces (chamber walls and uncoated top side of the wafers) was estimated to be 0.1. With these estimated values, a good agreement between DSMC predictions and experimental data was obtained, as will be shown below. The zinc layer thickness was determined from the steady state net number flux as found in the simulation, the zinc bulk density (7140 kg/m^3) and the duration of the experimental deposition (300 s).

The VSS collision model was used, the species parameters can be found in table 1. The DSMC parameters for the different simulations can be found in table 2. The simulations were assumed to have reached steady state after 0.2 s.

RESULTS

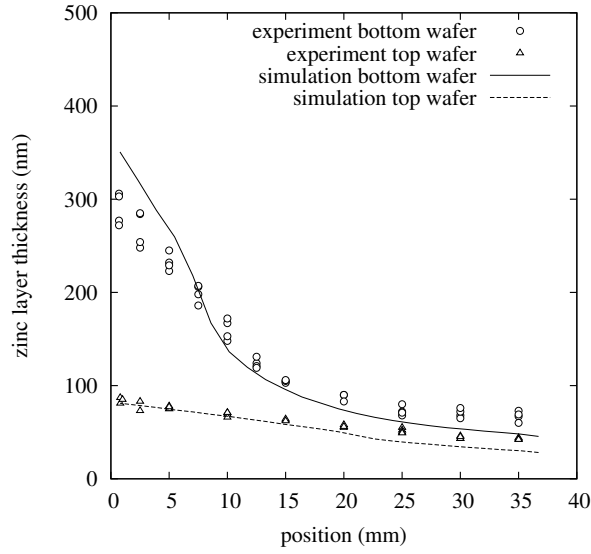
The results of the experiments and simulations can be found in figure 2. The position on the x-axis is measured radially from the edge of the hole in the wafer. The zinc layer thickness is presented as measured, *i.e.* this is the deposition in 5 minutes. Each figure contains the experimental and numerical results for the deposition on both the bottom and top wafer (on the side facing the zinc source). The experimental results consist of at most 4 measurements per wafer per location, as two trenches were etched in each wafer and two measurements are possible per trench. At some locations, less than four measurements are available, this occurs mostly near the center of the bottom wafers. In these cases, an accurate measurement was not possible, *e.g.* because the zinc layer was damaged.

The top wafer experimental data in figure 2(c) show an unexpected and probably erroneous result near the center. The measured thickness decreases steeply toward the center, where a slight increase is expected (as in the other 3 figures). This is most likely due to a slightly damaged zinc layer.

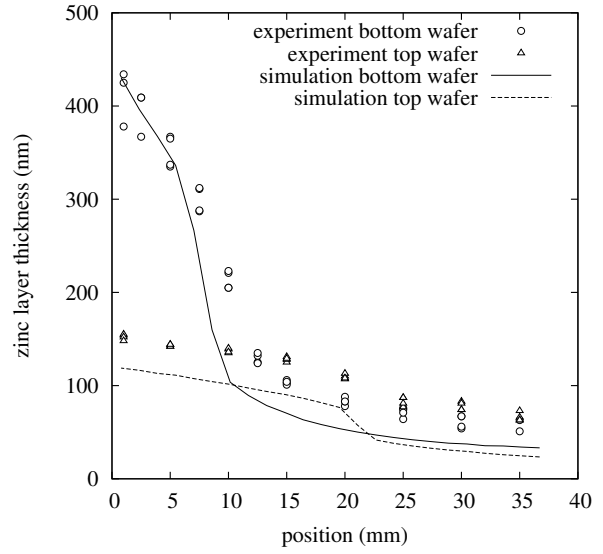
In general, the measurements and simulations compare very well, with both showing very similar trends. The transition in the profile on the top wafer clearly depends on pressure as expected, as can be seen by comparing figures 2(a), 2(b) and 2(c). Also, a dependence on the background gas can be observed by comparing figures 2(b) and 2(d).

The most important difference between the simulations and experiments is the tendency of the simulations to underpredict thin layers. The 'tail' of the bottom wafer and the entire top wafer simulation lines are almost always 25 to 50 nm lower than the experimental results.

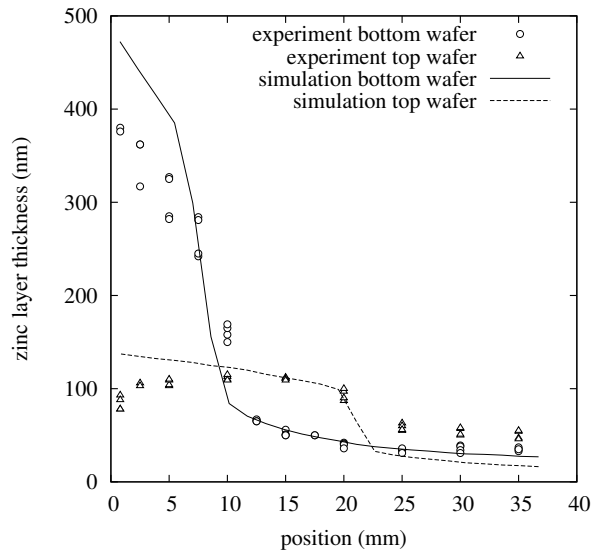
A possible explanation for this is the formation of a zinc oxide layer in the period between the opening of the vacuum vessel and the actual thickness measurement. The main oxide formed is zinc hydroxide ($\text{Zn}(\text{OH})_2$) [7] and the



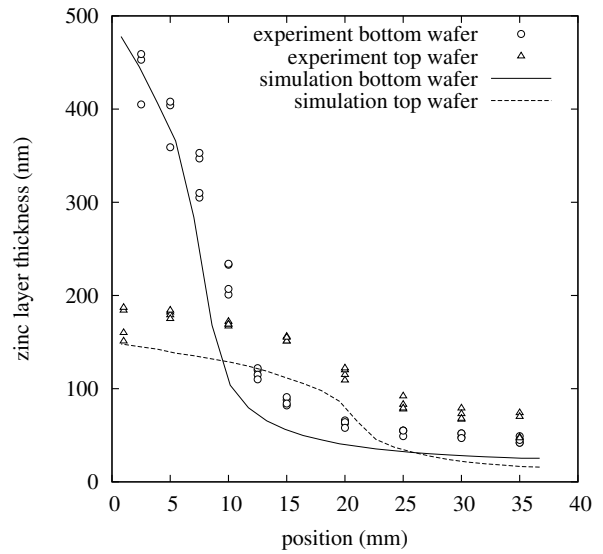
(a) Argon pressure of 0.25 Pa.



(b) Argon pressure of 0.088 Pa.



(c) Argon pressure of 0.031 Pa.



(d) Helium pressure of 0.088 Pa.

FIGURE 2. The experimental and numerical results for the four different experiments.

thickness of this oxide is 3.555 times the thickness of the unoxidized layer. The zinc corrosion rate (measured for one week and linearly [8] extrapolated to one year) is reported as $3 \text{ mg/cm}^2/\text{year}$ in an unpolluted laboratory atmosphere [7], which can be converted to a measured corrosion layer thickness of 80 nm after one week. In the present study, the corrosion time is approximately 2 hours and no oxide is removed or washed away (as assumed in [8]). In this case it is reasonable to assume diffusion limited corrosion, *i.e.* the corrosion rate decreases when the oxidation layer becomes thicker. The layer thickness is assumed proportional to the square root of time. The corrosion in 2 hours then becomes

9 nm, and the measured layer will be 22 nm thicker than the layer formed during the experiment.

Another possible explanation for the differences is the used values of the sticking coefficients. The simulations were performed using a fixed value for the sticking coefficient of 0.9 on the treated lower sides of the wafers, and a single fixed value of 0.1 on all other surfaces: the cold chamber walls (chrome coated copper), the shutter plate (aluminum) and the top side of the wafers (silicon). The results of the simulations were found to depend slightly on the precise value of the assumed sticking coefficients. For individual experiments, somewhat better agreement could be obtained by using the sticking coefficients as fitting parameters. Such a fitting exercise was not pursued. Furthermore, the sticking coefficients were assumed to be independent on *e.g.* zinc atom velocity. It is clear that the ratio between simulation and experimental results is highest near the center of the bottom wafer, indicating the possibility that the sticking coefficient is lower in this area, where the zinc atoms impact the surface with the highest average velocity. Also, the sticking coefficients need not be constant between consecutive experiments.

CONCLUSIONS

An experiment was performed to validate DSMC predictions of the deposition of a thin film. The experimental and numerical results show good comparison in trends, and reasonable comparison in terms of absolute values.

ACKNOWLEDGMENTS

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