An Approximate Method for Solving Unsteady Transitional and Rarefied Flow Regimes in Pulsed Pressure Chemical Vapor Deposition Process using the Quiet Direct Simulation Method

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Abstract. The Quiet Direct Simulation (QDS) method is a kinetic-based flux scheme that computes true-direction fluxes of mass, momentum and energy with high computational efficiency. In QDS, the molecular velocity is represented by the Maxwell-Boltzmann equilibrium distribution approximated by a Gauss-Hermite quadrature. The QDS algorithm is suitable for parallelization with its highly local nature. In this paper, the QDS method is used to simulate highly unsteady low pressure flows encountered in a Pulsed Pressure Chemical Vapor Deposition (PP-CVD) reactor. Two simulations were conducted to study the PP-CVD reactor flow field at 1Pa and 1kPa reactor base pressures. The time required to establish the quasi-steady under-expanded jet is found to be ~5ms, and the jet dissipates within 1ms of the end of injection. Simulation results also show uniform molecular arrival at the depositing substrate surface to promote uniform deposition. This important information is important to set up PP-CVD operating conditions as well as the reactor design. The assumption of the local Maxwell-Boltzmann equilibrium distribution used in the QDS scheme is then verified by examining the gradient length local Knudsen number based on the density, and by estimating the average number of particles collisions within each computational cell in one computational time step. The validity of local equilibrium assumption is found satisfactory at 1kPa reactor based pressure but not at 1Pa. However, the similarity of flow phenomena in both simulations suggests QDS to be a quick approximation method for low pressure flow simulations.

INTRODUCTION

Chemical Vapor Deposition (CVD) is a manufacturing technique which involves the formation of a thin solid film onto a substrate material through a chemical reaction of vapor-phase precursors. The industrial applications include electronic and machine components production, optical coating, and bio-medical implant manufacture. Conventional CVD systems operate with a continuous flow of precursor driven by chosen inert carrier gas with no significant pressure or concentration gradients in the reactor volume [1].

Pulsed Pressure CVD (PP-CVD) is an improved CVD technique developed by Versteeg *et al.* [2] and later, built and developed by Krumdieck *et al.* [3,4]. The novel PP-CVD system does not use a steady flow of the depositing precursor. Instead, it uses discrete timed injection of controlled amount of precursor solution at high supply pressure into a low pressure reactor chamber via an ultrasonic atomizer for liquid precursors or choked nozzle orifice for gaseous precursors. This unique precursor delivery system results a sharp spike in the reactor pressure at the end of the injection phase when the injection nozzle is shut. The reactor chamber is then continuously evacuated by a

vacuum pump until the reactor pressure resumes its base pressure before next precursor injection cycle. The injection and pump-down phases make up one PP-CVD process cycle which is repeated until a desired thickness of the thin film is deposited onto the substrate. Due to the rapid injection of the precursor solution into the continuously evacuated reactor chamber, the fluid density is significantly high near the inlet resulting large density gradient between the reactor's inlet and the exhaust. Thus, the fluid flow dynamics in the PP-CVD reactor fluctuates between rarefied and viscous flow during a PP-CVD process cycle within a short time period, which is generally of order 10s. The highly unsteady jet structures with large density gradients throughout the reactor cause the Knudsen number to vary from the continuum to the near-continuum or rarefied regimes.

The numerical study of the PP-CVD reactor flow field has been carried out previously [5] using the particle-based Direct Simulation Monte Carlo (DSMC) technique [6] which showed extremely computationally expensive due to the highly unsteady and complicated transitional flow in PP-CVD reactor. Because of the difficulty in obtaining converged solution with conventional Navier-Stokes solvers, a novel kinetic-based flux scheme named the Quiet Direct Simulation (QDS) method [7] is used to simulate the flow in the PP-CVD reactor chamber.

SECOND-ORDER AXISYMMETRIC QDS SCHEME

The QDS method is a novel kinetic-based flux scheme that computes true-direction fluxes of mass, momentum and energy by approximating the Maxwell-Boltzmann equilibrium distribution with a Gauss-Hermite quadrature. The second order $2N$ flux scheme presented by Smith et al. [7], later was extended to a second-order axisymmetric solver [8], is used in the present work. In QDS, the Maxwell-Boltzmann equilibrium velocity distribution function is discretised to a chosen number of N "velocity bins" (typically 3 or 4) in each spatial dimension. These velocity bins, representing the discretised molecular speed, are used to carry fluxes of mass, momentum and energy to travel between computational cells. The weights w_j of the Gauss-Hermite quadrature are used to calculate the mass fraction of the flux in each velocity bin while the associated molecular velocities are determined by the corresponding abscissas q_j. These true directional fluxes in each spatial dimension are then combined to create total of N^2 fluxes to be fluxed to the neighboring computational cells. Hence, for the present two-dimensional simulations with $j = 1,\ldots, J$ "velocity bins" in the x-direction and $k = 1,\ldots, K$ in the y-direction, the amount of mass m, velocity components v_x and v_y, and the energy ε carried in each velocity bin can be calculated from the gradient of density ρ, velocities u_x and u_y, and velocity variance $\sigma = \sqrt{RT}$, as following:

$$ m_{jk} = \frac{\left(\rho + \Delta x_L \dfrac{d\rho}{dx} + \Delta y_L \dfrac{d\rho}{dy}\right) V_c w_{xj} w_{yk}}{\pi} \tag{1} $$

$$ v_{xj} = u_x + \frac{du_x}{dx}\Delta x_L + \sqrt{2\sigma_v^2}\, q_j \;;\; v_{yk} = u_y + \frac{du_y}{dy}\Delta y_L + \sqrt{2\sigma_v^2}\, q_k \tag{2} $$

$$ \varepsilon_{jk} = \frac{(\xi - \Omega)\left(\sigma_v + \Delta x_L \dfrac{d\sigma_v}{dx} + \Delta y_L \dfrac{d\sigma_v}{dy}\right)^2}{2} \tag{3} $$

where V_c is the cell volume, Δx_L and Δy_L are the locations on the cell in the x- and y-direction, respectively, from where the flow properties are taken. For example, for a flux moving to the right of the cell center, $\Delta x_L = 0.5(\Delta x - v_{xj}\Delta t)$. ξ is the total number of degrees of freedom ($\xi = 2(\gamma-1)^{-1}$) and Ω is the number of simulated translation degrees of freedom.

These true directional fluxes are then transported to the destination neighboring cells determined by the velocity of the respective velocity bin. The amount of mass m, momentum p, and the energy E which fluxes to the destination cell can be calculated using Equation (4) to (6) as below:

$$ m_{flux,x} = \frac{v_{xj}\Delta t}{\Delta x} m_{jk} \tag{4} $$

$$p_{flux,x} = \frac{v_{xj}\Delta t}{\Delta x} m_{jk} v_{xj} \; ; \; p_{flux,y} = \frac{v_{yk}\Delta t}{\Delta y} m_{jk} v_{yk} \tag{5}$$

$$E_{flux,x} = \frac{v_{xj}\Delta t}{\Delta x} m_{jk}\left[\frac{1}{2}v_{xj}^2 + \varepsilon_{jk}\right] \tag{6}$$

The axisymmetric second-order flux-based QDS scheme [8] is used in present simulations which uses a regular cylindrical polar mesh. It should be noted that two important corrections are required since the volume of the cells varies with radial location. The calculation of the radial components of mass and momentum fluxes is corrected accordingly due to the change of cell volume in radial direction. Besides, an additional amount of momentum is added to the destination cell in the radial direction to account for the variation in the force due to static pressure across the top and bottom interfaces of an axisymmetric cell.

A maximum Courant–Friedrichs–Levy (CFL) criterion is used to reset the simulation time step Δt at each time step in order to prevent a particle from travelling more than a set fraction of the cell size, typically 0.5. This is to maintain the accuracy of the simulation in a discrete time.

In the current QDS algorithm, ghost cells are introduced to implement walls, stream boundaries, inflow and outflow boundaries. Fluxes crossing the wall boundaries are destroyed while ghost cells inside the wall having the same mass, momentum and energy except for a reversed flow direction normal to the wall are created. Ghost cells with properties equal to specified free stream conditions are created at inflow boundary. Absorb wall boundary is used at the outflow boundary in order to simulate the vacuum pump evacuation. This is done by omitting a fraction of the fluxes, which is determined based on the pump-down evacuation rate. The remaining fluxes are then reflected back to the flow field in a manner similar to the wall boundaries condition.

SIMULATION RESULTS AND DISCUSSION

In the present work, two sets of PP-CVD operating conditions are studied, which differ only in the reactor base pressures (the initial pressure of the reactor chamber when the injection begins). Both simulations were conducted using the axisymmetric second-order QDS solver with maximum CFL limitation of 0.5 and four QDS fluxes ($N = 4$) in each coordinate direction in a $2N$ flux scheme. Ideal helium gas at choked inlet flow conditions at 293K is injected into the reactor though an orifice. The initial reactor flow field is stationary with temperature of 293K. The reactor base pressure is 1Pa for Case I and 1kPa for Case II, respectively. Both simulations were carried out using 312,744 uniform square cells with 0.25mm cell size. Simulations with 0.125mm cells were carried out to determine that this is adequate to resolve the shock structure. Figure 1 shows the computational domain for both cases.
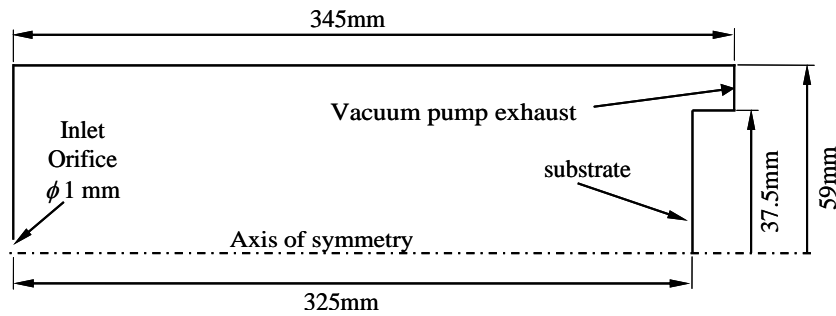

FIGURE 1. Schematic of PP-CVD reactor geometry.

Case I: PP-CVD Reactor Flow Field with 1Pa Reactor Base Pressure

The injection supply pressure for Case I is at 10kPa. Figure 2 shows the density contours plotted on a natural logarithmic scale of the PP-CVD flow field during a process cycle for Case I. Figure 2(a) shows the unsteady under-expanded jet development during first 5ms of the 0.1s injection phase while Fig. 2(b) shows the dissipation of the jet structure during the first 1ms of the pump-down phase.
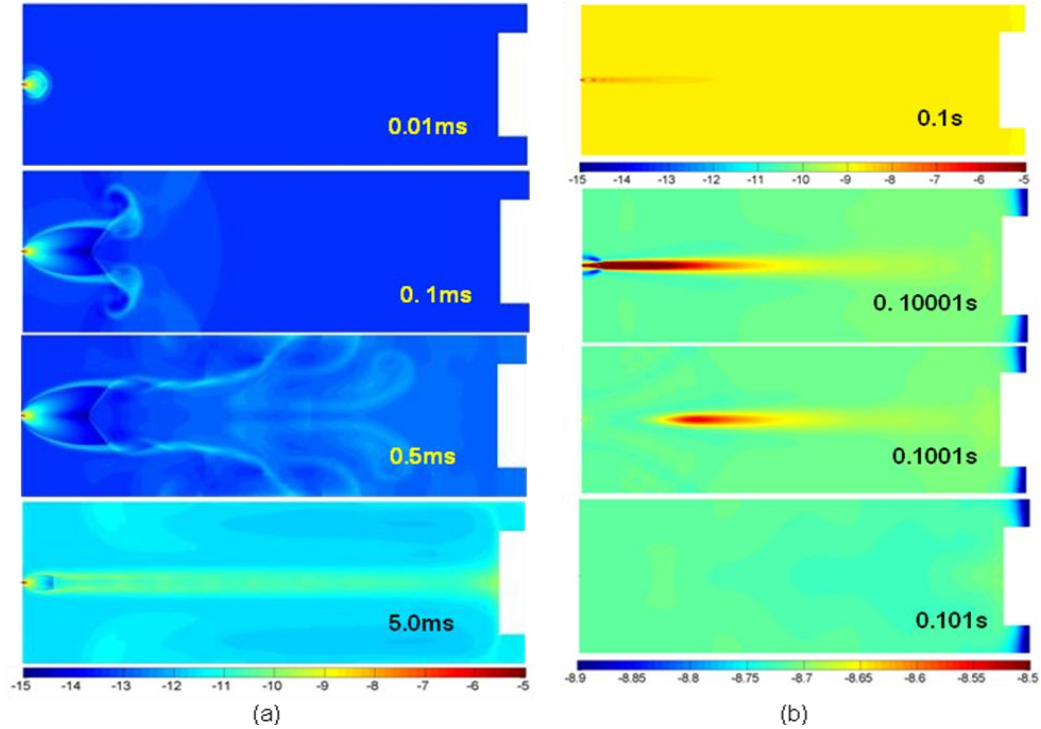
FIGURE 2. Log scaled density contour for the unsteady flow development in PP-CVD reactor at case I condition during (a) injection phase and (b) pump-down phase.

The shock structure and flow development is captured with far higher resolution and computational efficiency than the previous simulation [5] using DSMC method. This shows the capability of the QDS solver in modeling unsteady flows at low computational cost. During injection phase, a wide initial bow shock is initially generated at the exit of the inlet orifice, followed by travelling vortex roll-up and shock wave development patterns including the shear layer evolution and Mach disk formation. A quasi-steady under-expanded jet is formed after 5.0ms, which impinges onto the substrate region. At the end of the injection phase at 0.1s when inlet nozzle shuts off, the quasi-steady jet structure retracts towards the inlet nozzle without impinging on the substrate, which promotes uniform flow field condition near the substrate. This is a desired condition for precursor deposition to increase thin film uniformity. During the pump-down phase, the jet structure dissipates within about 1ms. The flow field is rather uniform during the remaining pump-down phase. Information on the jet formation and dissipation, especially the flow field structure near the substrate is useful for the design and choice of operating conditions for PP-CVD process.

Case II: PP-CVD Reactor Flow Field with 1kPa Reactor Base Pressure

The injection supply pressure for Case II is at 400kPa. Figure 3 shows the density contours plotted on a natural logarithmic scale of the PP-CVD flow field during a process cycle for Case II. Figure 3(a) shows the unsteady under-expanded jet development during first 4ms of the 0.1s injection phase while Fig. 3(b) shows the dissipation of the jet structure during the first 1ms of the pump-down phase.

The results in Case II shows, during the injection phase, an under-expanded jet with much narrower shock structure during the injection phase compared to that observed in the Case I. This may be caused by the higher initial reactor pressure, resulting in lower density gradient between the inlet and the initial reactor condition consequently lower rates of diffusion and pressure driven flow radially from the high concentration regions, at the inlet and on the centerline of the reactor, to the outer regions. This produces lower rates of mass transport radially outwards. Therefore, the jet expansion regime is smaller than that in Case I. During the pump-down phase, the jet structure again dissipates rapidly in about 1ms, after the inlet jet has been shut off at 0.1s, allowing a considerably uniform flow field to develop in the remaining pump-down process.
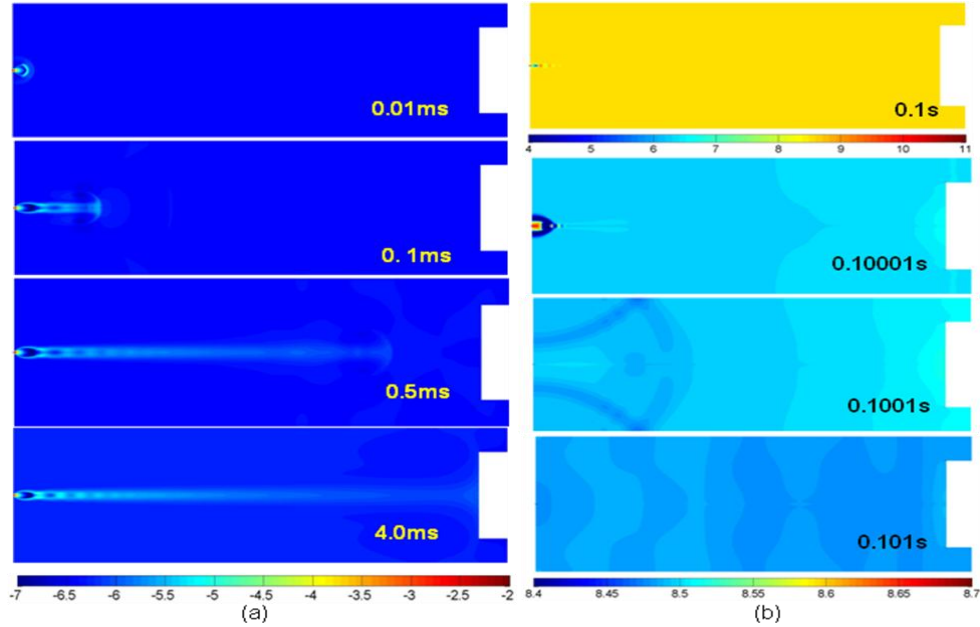
FIGURE 3. Log scaled density contour for the unsteady flow development in PP-CVD reactor at case II condition during (a) injection phase and (b) pump-down phase.

Uniformity of Molecular Arrival at the Substrate Surface

An important outcome of the numerical studies of the PP-CVD flow field is the quantification of the uniformity of the flow field near the substrate surface. As observed in the experimental work [4], the deposition rate and the thin film growth rate are very dependent on the molecular arrival rate at the substrate surface. This can be studied by determining the accumulated mass of the flow particles that is being transported to the substrate surface. Figure 4 shows the plots accumulated mass of precursor onto the substrate Case I at chosen time periods during the existence of the jet structure when the uniformity of the flow field near the substrate region is questionable. A substantially similar accumulated mass of precursor onto the substrate plot is also noticed in case II. As the simulation domain represents an actual cylindrical PP-CVD reactor, the annular surface area of the substrate increases as substrate radius increases. Hence, to justify the uniformity of the total mass onto the substrate surface, the accumulated mass over the annular surface area was computed and plotted. Both plots suggest considerable uniformity in the flow field near the substrate surface except near the center of the substrate which may due to the jet impingement on the substrate during the chosen time periods as well as a numerical error in the corner computational cell treatment.
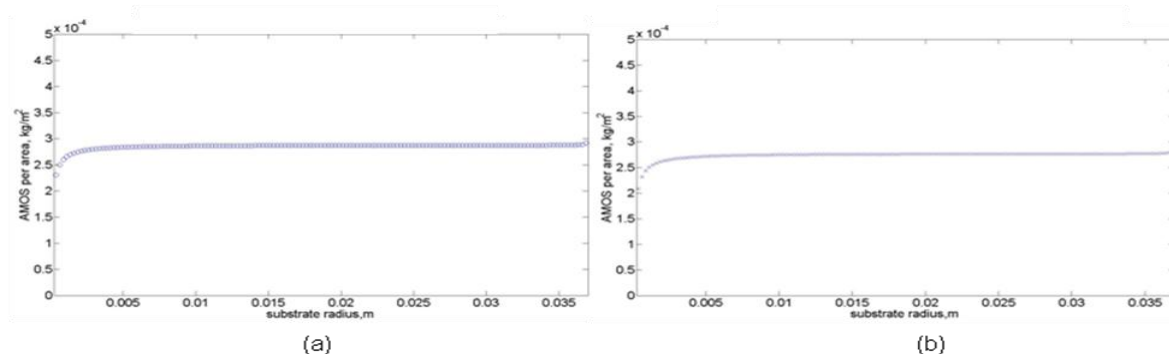

FIGURE 4. Accumulated mass of precursor onto substrate per area in the radial direction of the substrate disc during (a) first 5ms of injection phase in Case I, (b) first 5ms of pump-down phase in Case I

Validity check of the local equilibrium assumption in QDS method

The QDS method assumes that thermal equilibrium is established locally within each computational cell at each time step where the molecular velocity is in Maxwellian distribution. General speaking, thermal inequilibrium among the particles' energy modes occurs when the particles' collision rate becomes too low that the continuum condition breaks down in the expanding flow. Hence, to investigate the validity of the equilibrium assumption, the gradient length local Knudsen number (Kn_{GLL}) [9] was calculated. It is commonly considered that continuum breakdown occurs when $Kn_{GLL} \geq 0.05$ in the flow field. It is found that Kn_{GLL} based on density $(Kn_{GLL})_\rho$ is greater than 0.05 in Case I in the most of the shock regions indicating that the continuum assumption is invalid. In Case II, $(Kn_{GLL})_\rho$ is generally less than 0.05 except in some limited regions near the Mach disc in the shocks where $(Kn_{GLL})_\rho \approx 0.14$. However, these regions are unlikely to have significant effect on the flow development, indicating that the local density gradient within the computational cell was not large enough to move the particles downstream before thermal equilibrium is re-established. Thus, it is fair to assume that although continuum breakdown occur in a small region of the flow, QDS is capable of simulating a satisfactory approximation of the flow field of Case II.

The validity of the equilibrium assumption is also checked using the average number of particle collisions per computational cell per time step. The average particle collision time is first computed from the ratio of molecule's local mean free path to the average thermal velocity. Then, the average number of particle collisions is approximated from the ratio of the average time between particle collisions to the time step used. The difference between the physical non-equilibrium distribution and the equilibrium distribution becomes insignificant with at least two collisions per time step per particle for collision-limited DSMC [10]. From the simulation results, it is again noted that this condition is not satisfied anywhere in Case I. However, in Case II, the average number of particle collisions per computational cell per time step is generally greater than two throughout the flow field except, again, at region near the Mach disc. Thus, the assumption that equilibrium is re-established in each time step is justified for case II.

CONCLUSIONS

The axisymmetric, second-order QDS scheme has been used to simulate the flow field in the highly unsteady low pressure flow of a PP-CVD process. The results show that QDS is capable of providing a satisfactory quick approximation of flow field with high quality flow visualization. The validity of the local equilibrium assumption in QDS is acceptable at 1kPa reactor based pressure but not at 1Pa. The time taken to establish and dissipate the quasi-steady jet structure has been determined. The uniformity of the molecular arrival at the substrate surface has also been studied. This important information is essential for the design of PP-CVD reactors and operating cycle.

ACKNOWLEDGMENTS

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