Modeling of flow and heat transfer in a vertical reactor for the MOCVD of zirconium–based coatings

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Abstract

Flow and heat transfer in a vertical reactor used for the MOCVD growth of zirconium based compounds is studied by computational modeling. The verification of computational predictions is done by temperature measurements. Flow regimes are compared with respect to the flow structure and temperature distribution in the reactor. The modeling study results in better understanding of the processes that determine growth rate uniformity and reproducibility.

1. Introduction

The subject of the present work is the prediction of flow and heat transfer by numerical modeling including radiative transfer in a vertical reactor used for the metalorganic chemical vapor deposition (MOCVD) of thin layers of zirconium–based compounds. Recently MOCVD of zirconium–based layers has gained increasing attention in semiconductor device technology due to the fabrication of high dielectric constant and ferroelectric thin films like PZT ($Pb(Zr,Ti)O_3$) for memory device applications. In the present work the growth of materials like zirconium nitride (ZrN), zirconium carbonitride Zr(C,N) [1] and zirconia (ZrO_2) [2] is considered. They are applied for hard coatings of advanced machining tools, hard diffusion barriers in semiconductor devices and sensor or optical coatings.

For modeling of MOCVD in the described growth system a finite volume based computational fluid dynamics code developed for modeling of CVD processes is used [3]. The goal of the presented work is to demonstrate the capabilities of the developed modeling tool, and to understand the processes in the reactor in order to achieve reproducible growth results reliably.

2. Experimental

The reactor consists of a vertical quartz tube with the sample placed on a susceptor in its center. The susceptor is a circular resistively heated plate made of boron nitride–coated pyrolytic graphite. The dilute gas mixture of the carrier gas and the precursor is supplied through a stainless steel inlet tube inserted into the top of the reactor terminating closely above the heated susceptor. The novel and highly volatile precursor Zr(acac)$_2$(hfip)$_2$ is used. The inlet tube as well as the whole gas delivery system are heated to 100°C–150°C in order to prevent condensation of the precursor. The deposition is done at temperatures between T=400°C–800°C, at rather low pressures of P_0=0.5–10 mbar, and at total flow rates of Q=15–100 sccm. For the different materials to be deposited, two different gas mixtures are used, addressed as mixture 1 (50% He, 45% O_2, 5% H_2O) and mixture 2 (95% H_2, 5% NH_3). The temperature distributions at the reactor wall and the inlet tube were measured using a thermocouple.

3. *Modeling approach*

The modeling approach consists of computing the laminar, hyposonic (low Mach number) non–isothermal flow for a gas mixture with high temperature and density gradients. The gas transport properties are determined by Chapman–Enskog kinetic theory using Lennard–Jones molecular potentials, and their temperature and mixture dependence is taken into account. The two–dimensional, axisymmetric computational domain covers the reactor interior and walls without the reactor ambient. A finite volume method on block structured grids with boundary fitted coordinates, using the SIMPLE pressure correction algorithm, and a multigrid scheme for convergence acceleration is employed to solve numerically the system of partial differential equations [3].

An important issue is the accurate modeling of radiative heat transfer in the reactor which is the predominant heat transfer mode from the heated susceptor to the reactor walls and has a significant influence on the overall temperature distribution in the reactor. The heat transfer modeling approach is based on the exchange of radiative heat fluxes between the internal solid surfaces in the computational domain using diffuse view–factors. An entirely transparent gas mixture is assumed, diffuse reflection, emission and transmission at the semitransparent walls and the thermal interaction with the reactor ambient are considered. The strong spectral dependence of the optical properties of quartz is accounted for by multiband partitioning of the wavelength range of thermal radiation. The optical properties of the quartz walls are determined by considering the propagation of radiation in the walls including multiple internal reflection and absorption along its path. For details on the model see also [4] and references therein.

4. Results and Discussion

The employed modeling approach is validated by comparing the predicted temperature distribution at the reactor wall with the measured one. In figure 1 the fairly good agreement between experimental and computational results for the wall temperature profiles can be seen.

Various growth regimes are compared with each other by computational predictions. Emphasis is put on the following important issues: First the dependence of the flow structure on the selected process parameters, since growth results are affected by the formation of vortices above the susceptor; second, the dependence of the temperature level and profile at the susceptor surface on the process conditions, which has considerable impact on the deposition rate and its uniformity due to the strong temperature dependence of the kinetically limited growth process; third, the residence time of the precursor in the hot reactor zone above the heated susceptor, which is influenced by the temperature gradient and the flow velocity and determines the gas phase decomposition rate of the metalorganic precursor.

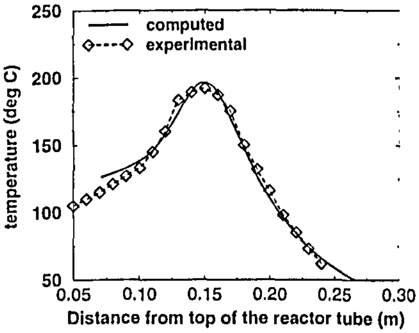

Fig. 1. Temperature distribution at the reactor wall. Gas mixure 2, total flow Q=45 sccm, p=5 mbar, T=550°C.

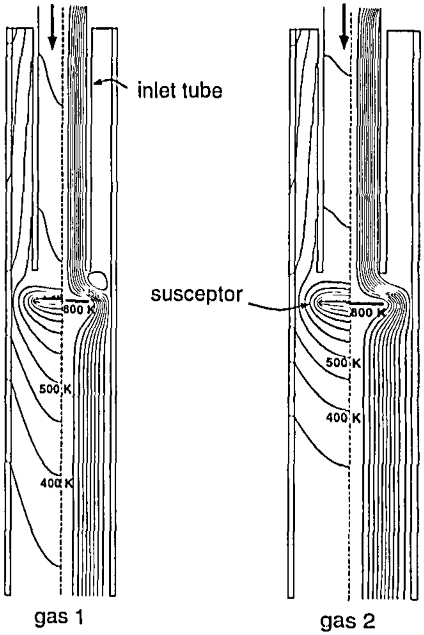

Fig. 2. Isotherms and Streamlines for both gas mixtures, Q=45 sccm, p=5 mbar, T=550°C.

The different transport properties of gas mixture 1 and 2 have significant impact on flow and heat transfer. Figure 2 shows streamlines and isotherms for the two gas mixtures at the same standard growth regime. The Reynolds number of mixture 1 is larger than that of mixture 2 by a factor of approximately 2.5 for the same process conditions resulting in a more pronounced formation of vortices due to separation at the opening of the inlet tube and downstream of the susceptor. Convective-conductive heat transfer in the gas flow and temperature profiles on the susceptor surface are affected by the composition of the gas mixture as well. The use of gas mixture 2 results in a more uniform temperature distribution on the surface of the heated susceptor than mixture 1 for the same conditions.

Changes in the total flow rate influence the temperature distribution at the susceptor surface, the intensity of vortices upstream and downstream of the susceptor and the steepness of the temperature gradient. Changes of pressure at a constant flow rate were found to have only little effect on the flow structure in the investigated pressure range of p=1–10 mbar. However, the temperature gradients above the susceptor are steeper and flow velocities are increased when the pressure is decreased at a constant flow rate. This corresponds to reduced residence times of the reacting gas mixture in the hot gas zone.

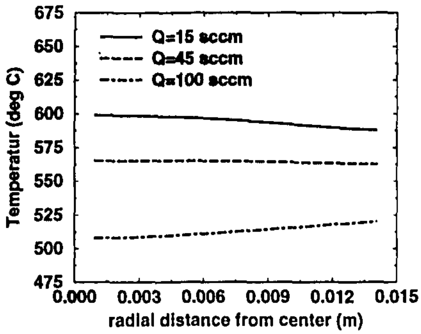

Fig. 3. Temperature distribution on the susceptor surface for various flow rates at constant heating, Q=15, 45, 100 sccm, p=5 mbar, T=550°C.

The formation of vortices is obviously related to separation rather than purely to buoyancy, which is effectively suppressed by the short distance between the opening of the inlet tube and the heated susceptor. The intensity and shape of vortices near the heated susceptor influences growth results directly by its impact on mass transfer of the growth determining chemical species and, indirectly, by modifying the heat transfer in the gas phase and temperature profiles on the substrate surface. Figure 3 shows that the temperature level on the susceptor surface is lowered and the temperature profiles are changed from a konvex to a koncave shape when the total flow rate is increased. This is partially related to the increased cooling rate by the impinging flow, partially to a small recirculation downstream of the susceptor that becomes more intense at larger flow rates and increases the cooling from below.

5. Conclusion

Growth of zirconium based compounds by MOCVD in a vertical reactor has been studied by numerical modeling of flow and heat transfer. Computational predictions are validated by temperature measurements at the reactor wall. Various growth regimes have been compared and the effect of growth conditions on the flow structure in the reactor and the temperature distribution on the susceptor have been studied. The results of the work were used for finding optimised process parameters.

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