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Numerical simulation and verification of gas transport during an atomic layer deposition process

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ABSTRACT

Atomic Layer Deposition (ALD) is a process used to deposit nanometer scale films for use in semiconductor electronics. The reactor consists of a warm wall horizontal flow tube, a substrate mounted on a disk downstream from the inlet, and cyclic flow between a reactant gas, a purging gas and a gas that preps the surface of the substrate. The objective is to achieve a uniform coating on the substrate layer by layer in minimal time. It is possible to use *in situ* monitoring of the gas phase and deposition to modify layer formation. Process improvement is currently accomplished experimentally by monitoring the precursor delivery and the growth of the film and adjusting the parameters: flow rates, temperature, pressure, concentrations, etc. Accurate simulation and optimization can decrease processing time and cost and increase control during product development. In addition, increased accuracy of gas transport simulation can be used to analyze reaction and diffusion rates, reaction mechanisms and other physical properties. In this paper we introduce the first comprehensive numerical solution of the Dusty-Gas Model including the complete binary diffusion term. We derive a concentration dependent Damkohler number relevant to the purge step of the process. The simulation matched the experimental data at a specific Damkohler number and further variation of the parameter confirmed existing experimentally observed phenomena.

1. Introduction

Reactive gas transport techniques are used for material processing including Chemical Vapor Infiltration (CVI) and Chemical Vapor Deposition (CVD). In this work, we introduce the first comprehensive numerical solution of the Dusty Gas Model to simulate gas transport. While the main purpose of the Dusty-Gas Model is to simulate flow through porous media, the theoretical formulation does not restrict it to this [1]. We use this model to capture binary diffusion and Fickian diffusion assuming a continuum in the gas phase. Continuum modeling is necessary to apply optimization techniques and derive non-dimensional parameters as opposed to Markov or other random walk modeling. We apply this innovative simulation to the Atomic Layer Deposition (ALD) process. ALD, a CVD technique, deposits single layers of atomic thickness resulting in precise thickness and shape. ALD is used to manufacture integrated circuit memory to conserve surface area and cost per bit. ALD can be a useful tool for scientific investigation using the two species, single-layer, self-limiting reactions to find both reaction rates and reaction mechanisms. A detailed model is necessary to optimize run time parameters to increase the quality of material production and decrease production time or run more targeted experiments.

In this section, we describe the physical setup of a single wafer atomic layer deposition process and present experimental parameters that define the relevant physical parameters in the model. In Section 2, we construct a model followed by a numerical scheme in Section 3. The purpose of the model is to predict the concentration

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of the chemical species in the reactor as a function of time and space in combination with *in situ* modeling that will lead to an optimal ALD process. In Section 4, we describe the experimental setup and discuss the relationship between the system and the model. This section also discusses the limitations of the model to batch processing and other industrial procedures. In Section 5, we compare the experimental results to the numerical results. In this section we also describe the purpose of the numerical scheme created and the insights gained from the solution of the general flow problem and the *in situ* modeling. Future expansions to the project are also discussed.

A typical ALD experimental reactor combines a warm-wall horizontal-flow tube, a substrate mounted downstream from the inlet, and alternating flow between a reactant, a purging and a second reactant gas. The reactions can be visualized as shown in Fig. 1 (for detailed reaction mechanisms see [2,3]). The illustration shows one reactant, entrained in a carrier gas, with preferential activation energy for bonding to the substrate, cf. Fig. 1 (a). The second step is the introduction of an oxidant that reacts with the previous reactant, cf. Fig. 1(b) forming a gaseous byproduct and depositing a metal oxide layer. This process is repeated where the reactant has a higher preference for reacting with the metal oxide layer over itself resulting in self-limiting deposition. The process creates a uniform coating on the substrate layer-by-layer. This leads to uniform layers being deposited by ALD on non-planar surfaces and high-aspect ratio surfaces [4,5]. The rate of growth of the layers is proportional to the repetition rate. The growth time is then the product of the number of cycles with the repetition rate for a given monolayer deposition and the total thickness is the number of cycles times the monolayer thickness.

A self-limiting process is desired and achievable but does not always result. For example, during the deposition of tungsten and molybdenum on silicon uneven coating and islands are created. During metal-oxide ALD on Carbon Nanotubes (CNTs) wetting is also a problem [6]. This problem has been addressed by reducing the residence time of the precursor according to its reaction mechanism. The residence time is constrained by concentration of gas arriving at the substrate as a function of time. One of the problems of thermally activated ALD in particular is that during inflow the reactants may decompose before arriving at the substrate [7]. After reaching the surface, a condition for a successful process is that the binding energy on the surface is much greater than the binding energy of subsequent layers [2]. This implies that the primary control parameters for ALD are the temperature of the substrate, the concentration and type of reactive gas near the surface [2,8]. Optimization using a numerical model should predict the reactive species as well as flow parameters to yield the desired coating in the least amount of time.

The reactor design studied here flows gas through a hot-walled CVD tube reactor. We use the recommendation from Suntola (1989) that a pressure of ~ 1 Torr is optimal to balance interdiffusion and entrainment [2]. With respect to Fig. 1(a), interdiffusion is the diffusion of the reactant gas around the carrier gas to the substrate, (cf. Section 2.6 on binary diffusion). Entrainment is the ability of the carrier/purge gas to affect the transport of the reactant/byproducts. If the pressure is too high, diffusion will be reduced, if the pressure is too low, entrainment will be reduced.

The model does not specifically address other methods of optimizing the residence time of the reactant gas including the use of flow control such as Synchronously Modulated Flow and Draw, cross flow, shower-head, and temperature control such as cold and hot-walled reactors [9,6]. To do this, one would need to modify the flow field and/or the boundary conditions for temperature. We also do not focus on optimization using pre-clean schedule and post deposition annealing [10].

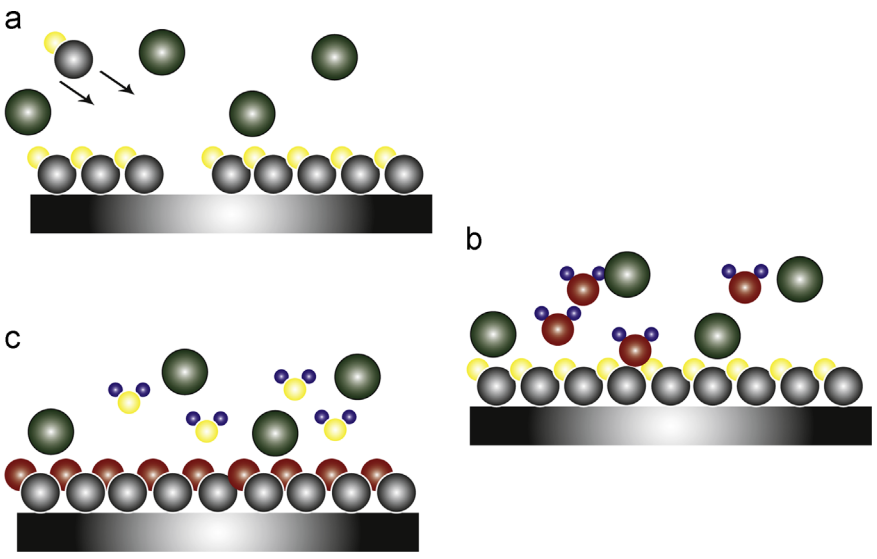

Fig. 1. This figure shows a typical metal-oxide ALD process. The first step is the deposition of a metal-precursor, carried by an inert carrier gas, onto a substrate(a). This is followed by the reaction of the metal precursor with an oxidant carried by the same carrier gas (b). The result is a metal oxide in a single layer (c). The inert carrier gas is also used to entrain and remove the excess reactants and reactant byproducts from the reactor.