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Effect of operation parameters on fines formation during thermal decomposition of silane

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ABSTRACT

This work presents a systematic numerical investigation of the effects of the operation parameters on silane pyrolysis in a chemical vapour deposition (CVD) reactor. A detailed chemical kinetic model of fines nucleation was coupled with the fluid flow, heat and mass transfer model. The commercial computational fluid dynamic (CFD) software FLUENT was used to predict the silane decomposition and fines formation. The effects of total reaction pressure, wall temperature, inlet gas composition, inlet gas velocity and specific surface area on the silane conversion and the fines formation have been investigated. The model was verified by comparing the simulated fines formation with the experimental data in the open literature. Results show that the total reaction presssure, inlet silane concentration and the wall temperature have vital effects on the fines formation, while the inlet gas velocity and the specific surface area have only influence in a certain range.

1. Introduction

High purity silicon for solar and electronic applications has been traditionally produced by the Siemens process from the hydrogen reduction of trichlorosilane. The process has many problems, such as low throughput, low thermal efficiency, and high electricity lost (Kojima et al., 1989). With silane (SiH_4) as precursor gas, the process has various merits over with trichlorosilane: higher yield, higher one-way conversation and lower deposition temperature. However, a frequent by-product during the pyrolysis of silane is the formation of fines from gas-phase chemical reactions in Siemens reactor (Lai et al., 1986) or fluidized bed reactor (FBR) (Filtvedt et al., 2010). Higher feed concentrations of silane, higher reaction temperature lead to more formation of fines via homogeneous nucleation.

The homogeneous nucleation limits CVD growth rate and causes contamination. Fines contamination is a leading cause of yield loss in CVD processing. Nijhawan et al. (2003) mentioned that more than half of the product yield losses in semiconductor manufacturing are from particle-induced defects. The fines are also a harmful source of contamination in fabrication of solid films (Talukdar and Swihart, 2004; White et al., 2006).

To radically understand of the chemical nucleation process, as well as subsequent particle growth, coagulation and transport, is necessary if we are trying to effectively control particle formation during silane pyrolysis. Various mechanisms for fines nucleation during silane pyrolysis have been proposed (Nijhawan et al., 2003; Kruis et al., 1994; Prakash et al., 2003; Körmer et al., 2010a, 2010b; Onischuk et al., 1997, 1998; Frenklach et al., 1996). Nijhawan et al. (2003) reviewed that these mechanisms can be roughly divided into two categories. One is based on the classical saturated vapour pressure theory, in which formation of supersaturated silicon vapour in the gas phase is taken as the driving force for nucleation during silane pyrolysis. The other one is based on the detailed chemical clustering model, in which the cyclic and polycyclic clusters are considered as the formation of particle nuclei in the gas phase. The second kind of model accounts for the experimental observation that particles formed during silane pyrolysis contain hydrogenated silicon groups rather than coalesced bulk silicon (Swihart and Girshick, 1999).

Some numerical models based on the detailed or simplified clustering model, have been developed to predict gas-phase nucleation, growth of silicon nanoparticles formed during thermal decomposition of silane (Slootman and Parent, 1994; Ring and O'Neal, 1992; Onischuk et al., 2000). The zero-dimensional flow model (Girshick et al., 2000) and the one-dimensional flow model (Kremer et al., 2003) were often chosen as the fluid flow model in these work. It has been demonstrated that there is a strong

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interaction exists between the hydrodynamics, the heat and reactive mass transfers, the homogeneous and heterogeneous reaction in a CVD reactor. Thus it is the vital important for capturing the complex phenomenon during silane pyrolysis to couple the cluster model with the detailed flow field models. Kommu et al. (2004) had used an aerosol dynamics moment-type formulation coupled with the 2D and 3D chemically reacting fluid flow models to predict particle concentration and size. More researches only paid attention on the gas-phase nucleation mechanism. Less attention was paid to the effects of the operation parameters on fines formation.

In this work, a reaction flow model coupled with detailed chemical kinetic model of particle nucleation proposed by Swihart and Girshick (1999), Girshick et al. (2000) and Bhandarkar et al. (2000) was set up to predict particle nucleation in a tube CVD reactor. It included: homogeneous reactions of gaseous intermediates (41 reactions), heterogeneous reactions of gaseous molecules on surface of reactor wall (10 reactions), gas momentum, heat and mass transfer. The model was used to investigate numerically the influence of the operation parameters (such as total reaction pressure, inlet velocity, inlet silane concentration) on the mount of the particle formed during silane pyrolysis. The CFD software FLUENT was utilized to solve the model. The model developed in this work was validated with original experimental data in the literature.

2. Transport models

2.1. Geometry model

In order to decrease the computation and storage load, a two-dimensional (2-D) model coupled with gas phase reaction and surface reaction was considered for a tube CVD reactor. The reactor is 200 mm in length and 10 mm in width. A mixture of silane and H_2 enters the reactors at the inlet. The side walls are held at a fixed temperature. The silane gas decomposes heterogeneously and homogeneously. Finally, the reactant and product gases leave the reactors through the outlet, which is fixed at atmospheric pressure.

2.2. Hydrodynamic model

The model involves four primary governing equations: mass conservation (or continuity), momentum conservation, energy conservation, and species conservation. The conservation equation for gas reaction flow is described briefly in Table 1. A more detailed description of the governing equations can be found in our early paper (Zhang et al., 2011).

2.3. Reaction model

During the last years, a great effort was devoted to the comprehension of the reactions involved in silicon deposition. Our model for the clustering process in silane plasmas was based on the mechanism developed by Swihart and Girshick (1999), Girshick et al. (2000) and Bhandarkar et al. (2000) for the clustering of intermediate species in atmospheric pressure thermal CVD of silicon from silane. The silicon hydrides were classified as silanes, silenes (suffixed with the letter A) and silylenes (suffixed with the letter B). The silylenes are isomers of silenes with two non-bonding electrons. The surface chemistry kinetics and some gas chemistry kinetics for intermediate species containing one or two silicon atoms was compiled by Ho et al. (1994).

The method proposed by Bhandarkar et al. (2000) was adopted to handle the fines. The maximum cluster size considered in this mechanism was five silicon atoms. All reactions leading to clusters with more than five Si atoms were considered irreversible. These clusters with more than five Si atoms were classified as 'fines'. This critical size is presently just a coarse estimate, but in the future can hopefully be obtained from the automated mechanism generation method. The overall mechanism is summarized in Table 2.

Table 1
Conservation equations.

Conservation equation type	Equation form
Continuity	$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0$
Momentum	$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i + F_i$
Energy	$\frac{\partial}{\partial t}(\rho E) + \frac{\partial}{\partial x_i}(u_i(\rho E + p)) = \frac{\partial}{\partial x_i}\left(k_{eff}\frac{\partial T}{\partial x_i} - \sum_{j'} h_{j'} J_{j'} + u_j(\tau_{ij})_{eff}\right) + S_h$
Species	$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \vec{J}_i + R_i$

2.4. Gas properties

The thermal conductivity of the gas species may be calculated from idea-gas-mixing-law. Mixture gas density was estimated based on the ideal gas law. The mass diffusion coefficients in the mass conversation were calculated by the formula of the molecular kinetic theory of gases with use of the Lenard-Jones 6–12 potential. The coefficients of the specific heat capacity polynomial and the Lennard-Jones parameters (the characteristic energy and the collision diameter) for the silicon cluster containing one or two silicon atoms were taken from Ho et al. (1994). For large silicon hydride clusters in the system, a group contribution method (Constantinou and Gani, 1994) was used to predict their thermochemical properties, Klincewicz and Reid simple method (Reid et al., 1987) was used to estimate their Lennard-Jones parameters, which are listed in Tables 3 and 4, respectively.

2.5. Turbulent model and numerical method

Reynolds numbers in CVD reactors are usually quite low. But a quite large temperature difference (up to 800 K) can lead to significant interactions between forced and free convection in the CVD equipment. Thus, the k-ε turbulent model was used to simulate the turbulent transport. The governing equations coupled with the boundary conditions have been solved using a commercially available software package FLUENT. The segregated solution algorithm has been selected. For the pressure-velocity coupling, the SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) method was used. The second-order upwind QUICK scheme are used to discretize the convection term in the model. All of the numerical tests are carried out to evaluate the effect of mesh size on the calculated results. The maximum relative difference is 9.6% and the maximum root mean square difference is 8.4%. The computational grid is defined by hexahedral cells, non-uniformly distributed.

The numerical stiffness of the multi-dimensional multi-species transport coupled with detailed CVD chemistry models leads to poor convergence, excessive computation time, and unreliable predictions. Thus, the stiff chemistry solver was chosen to approximate the reaction rate in the species transport equations. A convergence criterion of 1×10^{-06} was used for continuity, momentum, energy and species transport equations. Computation time for a complete flow field, species and aerosol simulation was approximately 60 h on a high performance SGI Octane workstation.

2.6. Boundary condition

At the inlet, the velocity distribution is considered uniform; the gas feed is assumed to be uniform at 300 K. The mass fraction of the species in the inlet is specified. A no-slip and a temperature condition are imposed on the side walls, respectively. Some rea-