# CFD Research Corporation

3325 Triana Blvd. • Huntsville, Alabama 35805 • Tel.: (205) 536-6576 • FAX: (205) 536-6590 • info@cfdrc.com

CFDRC


# PARTICULATE CONTAMINANT FORMATION AND TRANSPORT IN MICROELECTRONIC MANUFACTURING PROCESSES

Phase II Quarterly Report


by

Phillip J. Stout and Anantha Krishnan

CFD Research Corporation

and

N.P. Rao and S.L. Girshick

University of Minnesota





May 1997

CFDRC Report: 4396/5





This material is based upon work supported by the

Defense Advanced Research Projects Agency

Electronics Technology Office

DARPA Order No: D507

Program Code No: 5502

Issued by DARPA/CMO under Contract: MDA972-96-C-003

# 1. INTRODUCTION

This is the fifth quarterly report documenting the work performed during a two year Phase II STTR activity entitled "Particulate contaminant formation and transport in microelectronic manufacturing processes." The overall objective is to produce a charging, transport, and growth simulation (CTGS) tool that can be used effectively by equipment manufacturers and users to reduce particle generation in fabrication systems. The project includes collaborations with Prof. Steven Girshick (University of Minnesota) on ion induced nucleation and Prof. Mark J. Kushner (University of Illinois) on particle charging and transport.

## 1.1 Project Objectives

The work to be performed in this Phase II STTR includes:

1. To obtain and adapt models for particle charging, particle growth, and electrostatic and ionic drag forces on particles from Prof. Mark J. Kushner's group at the University of Illinois Urbana-Champaign (UIUC).

2. To obtain and adapt models for ion-induced nucleation from Prof. Steven Girshick's group at the University of Minnesota (UMN).

3. To implement the above models into CFDRC's reactor model, CFD-ACE, to obtain solutions for local particle formation and transport in conjunction with other macroscopic processes such as fluid flow, heat/mass transfer, plasma transport and chemistry.

4. To perform detailed parametric studies to assess the effects of various operating conditions on particle formation and transport.

5. To demonstrate the integrated model in collaboration with an equipment manufacturer to reduce/eliminate particle effects in a processing system.

6. To transfer the technology to the industry in collaboration with SEMATECH and its member companies.

7. To prepare a final report documenting the work performed during the Phase II study.

## 1.2 Project Status

The charging, transport, and growth simulation (CTGS) tool's graphical user interface (GUI) has undergone further development. The portion of the GUI handling the charging and transport portions of the tool is nearing completion. The basic tools have now been established with future work focusing on making it commercial grade. The moment model used for the growth aspect of the tool has undergone further development.

## 1.3 Overview

Section 2 describes activity in GUI development and GUI solver coupling. Section 3 describes progress made modeling nucleation pathways for use with the moment model as reported by the sub-contractor. Section 4 discusses the future plans for the CTGS tool development.

# 2. GUI DEVELOPMENT OF PARTICLE CHARGING AND TRANSPORT

A graphical user interface (GUI) for the CTGS tool is undergoing further testing. Some modifications that were a result of the testing include:

- The toolbox portion of the GUI is updated assuring that all frames controlled by variables are packed properly when reading in a new model file.

- Data entered into an entry box is checked for integrity. Checks are made for type (real, integer, character), as well as maximum and minimum values. If a number entered is out of range it will be replaced by the specified maximum or minimum number. If no maximum or minimum for a variable is desired it can be set to nil which will set no limit on the data value entered.

- Output to entry boxes is now formatted.

- The progress of calculation is now graphed using a tk canvas widget. The graph tracks particle number and average velocity versus simulation time. The graph has self adjusting axis values.

- Version control and a time stamp were added to GUI.

- The current working directory is now changed to the location of the model file (.nam) so fortran output files get written to the same location as the model file as opposed to wherever the gui was initially called.

- A routine has been written to handle inputting the more generic PFG file format where the i, j, and k indice do not necessarily line up with the x, y, and z-axis, respectively.

- The application can now be stopped before the scheduled end and have all necessary result files generated. This is achieved by using a signal file which the main application queries every iteration loop.

- The dual roles of the dtmaxstep variable were separated. The variable was used to control the burst period as well as the period between writes to the SPY file.

- The inner loop timing mechanism was rewritten to run on a global clock instead of relying on integer loop values. Using global clock allowed a reorganization of timed events and particle introduction during the simulation.

## 3. MOMMENT MODEL

The following is a report written at the University of Minnesota documenting work done on the nucleation term to be included in the moment model described here and in earlier reports.

### 3.1 Introduction

This report documents the progress made during the fifth quarter of the Phase II STTR study titled "Particulate Contaminant Formation and Transport in Microelectronic Manufacturing Processes". The objective of this project is to transfer/adapt particle nucleation models developed at the University of Minnesota and incorporate them into the macroscopic reactor flow and plasma models developed by CFDRC. The combined code will provide a comprehensive computational tool to simulate various interactions (between gas species, charge carriers, and dust particles) during microelectronic fabrication processes and to facilitate the analysis/optimization of industrial reactors.

### 3.1.1 Need for Numerical Modeling

Particle contamination currently occurring in microelectronics fabrication processes has been understood and controlled largely through empirical methodologies and post-process observation/analysis. The sources of particle contamination can be attributed to feed gases, gas phase reactions, and solid surfaces. The remedy methods have been developed through hardware experimentation. Contaminant formation, growth, and transport in neutral and charged gas environment involve many complicated phenomena such as nucleation, coagulation, diffusion, convection, condensation, evaporation, ionization, and interactions between particles, molecules, atoms, ions, and electrons, as well as these particles' interaction with external force fields. It is difficult to understand, through hardware experimentation or purely theoretical analysis, the effect of mutual interactions between these phenomena over a range of operating conditions. The sizes of the particles generated in plasma systems are of the order of a micron or smaller. It is difficult to observe and measure the formation and transport of these particles even with the aid of highly sophisticated visualization equipment. The underlying physics and chemistry governing the particles' behavior in plasmas have not been completely understood yet. As a result, it is prohibitively expensive and time consuming to experiment with process design and equipment development. In this regard, numerical simulations can be a very effective tool to model, in a systematic manner, the influence of various operating parameters on particle formation, growth, and transport plasma systems. Such a model can be used to understand the many complex and coupled interactions in plasmas, to interpret experimental measurements, and to predict the behavior of the particles.

Although for many years, some fundamental modeling work has been done to address issues of particle formation in areas such as air pollution, clean-room contamination, particle generation, powder production, and industrial atomization. In most studies, phenomena such as nucleation, transport, conservation, kinetics and discharges are often treated separately. No attempts have been made to integrate a particle model with general purpose reactor models. There is currently a need for coupling particle, plasma, flow, and chemistry models with reactor simulations in order to facilitate reactor design. This approach will benefit a large number of industrial users. In order to simulate particle behaviors in plasma processing over a range of operating conditions, a numerical model should have the following features:

a. the ability to model flow in complex reactor geometries with arbitrary boundary conditions;

b. submodels for gas-phase and plasma chemistry; and

c. submodels for aerosol dynamics including particle nucleation and growth.

The application of advanced numerical models will result in improved micro-contamination free processes and novel equipment designs for semiconductor device fabrication.

## 3.2 Project Objectives

The overall objective of the proposed work is to develop and transfer advanced computational codes for particle nucleation and growth from the University of Minnesota to CFDRC. These models will be integrated into an existing Computational Fluid Dynamics (CFD) code capable of solving gas phase transport and chemistry in complex reactor configurations. A low-pressure plasma reactor model has been preliminarily developed at CFDRC and is subjected to refinement and completion pending further funding. The combination of these three categories of codes will result in the development of a overall (comprehensive) computational tool that simulates interactions between fluid flow, discharges, and particulates over a range of operating conditions.

Our specific goal for the Phase II STTR is to develop and transfer realistic models of particle nucleation and growth under conditions representative of microelectronic manufacturing processes. These may include such processes as homogeneous nucleation, ion-induced nucleation and chemical nucleation, i.e. nucleation resulting from chemical reactions of gas-phase precursor species.

## 3.3 Project Status

The following tasks have been accomplished in meeting the goals of the Phase II STTR study: An atomistic modeling framework has been developed for calculation of particle nucleation rates in microelectronics manufacturing processes. Classical nucleation theory[1-4] is based on the "capillarity" approximation, i.e., the assumption that small clusters are "liquid" droplets whose properties equal their values for the bulk liquid, and also presupposes the existence of a condensable vapor. However, this approach is not suitable for treating nucleation in microelectronic fabrication processes, where the critical cluster size is often very small, and in some cases the nucleation proceeds via chemical reactions between gas phase radical species in the absence of a supersaturated vapor. In

the atomistic approach[5-7], nucleation rates are calculated based on the properties of small discrete clusters, which eventually grow to large aerosol particles. The nucleation rate expression obtained from this approach is in the form of a summation over discrete cluster properties. The summation converges rapidly around the critical cluster size, which is often as small as a few atoms. Summation expressions may be derived for all possible mechanisms of particle nucleation including homogeneous nucleation, ion-induced nucleation, and chemical nucleation. This approach allows the direct utilization of experimental and/or computational data for cluster properties, which are known to be poorly approximated by the traditional "capillarity" model. Sample calculations have been performed for the nucleation of silicon particles in microelectronics fabrication processes assuming various nucleation scenarios including (1) homogeneous nucleation from silicon vapor; (2) condensation of neutral silicon vapor onto silicon anions, for conditions representative of silicon PECVD; and (3) polymerization of silicon hydride species under conditions representative of silicon LPCVD and PECVD processes. The nucleation rates derived from these atomistic approaches may be used as particle source terms in moment models of aerosol dynamics being developed by CFDRC.

### 3.4 Summary of Recent Results

In past quarters, we have explored several clustering pathways (including homogeneous nucleation of silicon vapor, ion-induced nucleation of $Si^-$ anions, and chemical nucleation routes) for the formation of particles in LPCVD and PECVD systems used for depositing silicon from silane precursor. In the recent past, however, there has been considerable experimental evidence that the formation of particles in silicon deposition systems proceeds through gas-phase chemical reactions involving hydrogenated silicon cluster, i.e. silicon hydrides[8-13]. Several reaction sequences involving silicon hydride species have been proposed, including those involving, neutral radicals, and even cations. Of these the reaction pathway appearing to have the strongest experimental support is the anion clustering route[10,11] of the form:

$$Si_{n-1}H_{2n-1}^- + SiH_4 \Leftrightarrow Si_nH_{2n+1}^- + H_2 \qquad (1)$$

for n=1,2,3...Nucleation rates for this reaction sequence have been previously calculated using the atomistic theory for hydrogenated clusters containing up to 5 silicon atoms. Thermodynamic property data for these clusters are now available in the literature[14].

In this report we present results from alternative chemical nucleation scenarios involving neutral species. Two possible reaction sequences for silicon have been proposed in the literature, and could apply to both PECVD as well as LPCVD processes[8,9,12]:

$$Si_{n-1}H_{2n} + SiH_2 \Leftrightarrow Si_nH_{2n+2} \tag{2}$$

$$Si_{n-1}H_{2n-2} + SiH_4 \Leftrightarrow Si_nH_{2n} + H_2 \tag{3}$$

Following the usual formulation of the atomistic nucleation theory[7] for chemical nucleation, nucleation rates may be calculated using expressions of the form (for Reaction 3),

$$J = N_{SiH_2} N_{SiH_4} \left\{ \sum_{i=1}^{M} \left[ k_i \left( \frac{N_{SiH_4}}{N_{H_2}} \right)^{i-1} \exp\left( \frac{\Delta_f G_i^o}{k_B T} \right) \right]^{-1} \right\}^{-1} \tag{4}$$

Figure 1 shows calculated nucleation rates versus temperature for concentrations reasonably representative of silane PECVD and LPCVD ($N_{SiH^2} = 10^{11}$ cm$^{-3}$, $N_{SiH^4} = 10^{15}$ cm$^{-3}$) using the various chemical nucleation model expressions. For the case of reactions (1) and (3), the "driving force" $\alpha = \frac{N_{SiH_4}}{N_{H_2}}$ was assumed to be unity. Approximate rate constants for the clustering reactions (1) to (3) have been reported in the literature[11,12], and have been used in these calculations.

From Figure 1 it is seen that at lower temperatures ($T$ < 1000 K), the atomistic rates of chemical nucleation depend strongly on the reaction sequence. The neutral reaction sequences yield higher nucleation rates, and thus appear to be viable even in PECVD processes. However, it must be noted that the nucleation rates also depend on the concentrations of the "growth" species and the "initiating" species participating in these reactions. At present, these values have been estimated, and may be inaccurate by several orders of magnitude. In order to draw conclusions regarding the most likely nucleation route, it is necessary to couple the atomistic nucleation models presented here to gas-phase chemistry models being developed by CFDRC.

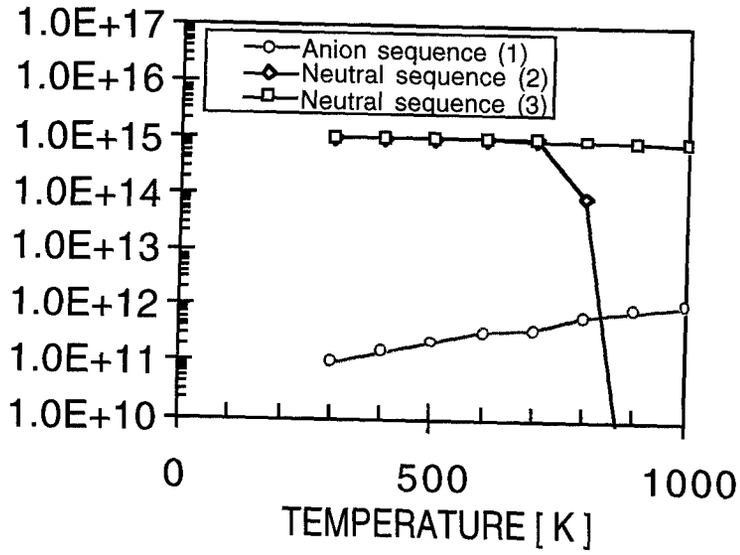


Figure 3-1. Calculated Nucleation Rates of Silicon from Chemical Reaction Pathways

## 4. FUTURE WORK

The atomistic approach to calculating nucleation rates has been extended to clustering reaction sequences involving neutral hydrogenated clusters of silicon. The next step is to integrate these atomistic expressions into aerosol dynamics models, e.g. a moment model[15] capable of accounting for other processes such as particle growth, particle charging and neutralization, particle transport and deposition onto reactor walls.

The current status of the project is shown in Table 4-1. Future work will address both areas of the technology transfer focusing on improvements to the transport, charging, and growth models.

The moment model will undergo further development to incorporate the atomistic nucleation model as a source term. The possibility of forming a discrete-modal model will be explored. A discrete-modal model solves separate General Dynamic Equations (GDEs) for small clusters and the moments of the GDE assuming a lognormal size distribution for particles above a specified size. Coupling a discrete model with a moment model will be explored as an option.

Table 4-1. Status of Project Tasks

| Task Description | Months After Receipt of Contract |
|---|---|
| | 2 4 6 8 10 12 14 16 18 20 22 24 |
| Task 1. Model Transfer from UIUC | |
| (i) Model Transfer | |
| (ii) Documentation | |
| (iii) Consultation on Model Adaptation | |
| Task 2. Model Transfer from UMN | |
| (i) Ion-Induced Nucleation Model | |
| (ii) Model Documentation/Transfer | |
| (iii) Consultation on Model Adaptation/Coupling | |
| Task 3. Physical Model Development and Adaptation at CFDRC | |
| (i) Model for Particle Formation | |
| (ii) Model for Particle Transport | |
| (iii) Adaptation of UIUC and UMN Models | |
| Task 4. Coupling with CFD Code | |
| (i) Incorporation of Models into CFD Code | |
| (ii) Testing and Assessment of Coupled Model | |
| (iii) Preliminary Validation Studies | |
| (iv) Parametric Studies | |
| Task 5. Packaging and Documentation of Coupled Model | |
| (i) Implementation of Graphical User Interface (GUI) | |
| (ii) Detailed Documentaition of Models and Code Structure | |
| (iii) Preparation of Final Report | |

The GUI for the charging and transport will undergo further testing. More efficient information sharing from ACE and PLASMA(ICP) code to the transport code will be explored such as through the restart files. The transport model which currently assumes monodisperse systems will be altered to transport more than one particle size at the same time. Other modifications which have yet to be finalized could include transport of non-spherical particles (i.e., flakes), accounting for particle coulomb-coulomb interactions, making particle charging time-dependent, changing the charging model for smaller size particles, and allow for variance in size as particles collide with each other increasing in size or atoms evaporate off of the particle reducing its size.

## 5. REFERENCES


1. Becker, R. and Döring, W. Ann. d. Phys. **24**, 719, 1935.
2. Volmer, M. and Flood, H., Z. Phys. Chem. A **170**, 273, 1934.
3. Tohmfor, G. and Volmer, M., Ann. Phys. (Leipzig), Ser. 5 **33**, 109, 1938.
4. Volmer, M., *Kinetik der Phasenbildung*, Theodor Steinkopff Verlag, Dresden, 1939.
5. Girshick, S. L., Rao, N. P., and Kelkar, M., J. Vac. Sci. Technol. **A 14(2)**, 529, 1996.
6. Kelkar, M., Rao, N. P., and Girshick, S. L., Proc. 14$^{th}$ Int. Conference on Nucleation and Atmospheric Aerosols, Helsinki, Finland, Aug. 26-30, 1996.
7. Girshick, S. L., accepted J. Chem. Phys., 1997.
8. Onischuk, A. A., Strunin, V. P., Ushakova, M. A., and Paniflov, V. N., J. Aerosol Sci. **28**,207 1997.
9. Slootman, F. and Parent, J. C., J. Aerosol Sci. **25**,15,1994.
10. Choi, S. J., and Kushner, M. J., J. Appl. Phys. **74**, 853, 1993.
11. Howling, A. A., Sansonnens, L., Dorier, J.-L., and Hollenstein, C., J. Appl. Phys. **75**, 1340, 1994.
12. Sato, N., Shirantani, M., and Watanable, Y., Jpn. J. Appl. Phys. 33,4266, 1994.
13. Perrin, J., Böhm, C., Etemadi, R., and Lioret, A., Plasma Sources Sci. Technol. **3**, 252, 1994.
14. Katzer, G., Ernst, M.C., Sax, A. F., Kalcher, J., submitted to *J. Chem. Phys.*, 1997.
15. Friedlander, S. K., Ann. New York Acad. Sci., **404**,354, 1983.