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Multiscale systems engineering with applications to chemical reaction processes

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Abstract

New applications in materials, medicine, and computers are being discovered where the control of events at the molecular and nanoscopic scales is critical to product quality, although the primary manipulation of these events during processing occurs at macroscopic length scales. This motivates the creation of tools for the engineering of multiscale reacting systems that have length scales ranging from the atomistic to the macroscopic. This paper describes a systematic approach that consists of stochastic parameter sensitivity analysis, Bayesian parameter estimation applied to ab initio calculations and experimental data, model-based experimental design, hypothesis mechanism selection, and multistep optimization.

Keywords: Multiscale system; Stochastic simulation; Stochastic optimization

1. Introduction

New applications in materials, medicine, and computers are being discovered where the control of events at the molecular and nanoscopic length scales is critical to product quality, although the primary manipulation of these events during processing occurs at macroscopic length scales (e.g. temperature of the system, valves on flows into and out of the system, applied potential between two electrodes). These applications include nanobiological devices, micromachines, nanoelectronic devices, and protein microarrays and chips (Drexler, 1992; Hoummady and Fujita, 1999; Lee et al., 2003; Prokop, 2001; Sematech, 2003; Tsukagoshi et al., 2002). While many of these devices are designed using highly simplified models or trial-and-error experimentation, recent advances in computer speed and memory, numerical algorithms, and sensor technologies suggest that a more systematic approach to the design and control of these devices is possible.

The potential applications motivate the creation of tools for the engineering of multiscale reacting systems that have length scales ranging from the macroscopic to the atomistic. This paper describes the challenges to building such multiscale systems tools, which include uncertainties in the physicochemical mechanisms as well as the values of thermodynamic and kinetic parameters, high computational cost in the simulation of model equations that can span a wide range of time and length scales, lack of manipulated variables and direct measurements of most properties at the nanoscale during processing, and the inapplicability of most existing systems engineering tools to address systems described by noncontinuum and dynamically coupled continuum-noncontinuum models.

This paper describes an emerging approach to addressing these challenges to the engineering of multiscale reacting systems that consists of stochastic parameter sensitivity analysis, Bayesian parameter estimation applied to ab initio calculations and experimental data, model-based experimental design, hypothesis mechanism selection, and multi-step

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optimization. This enables multiscale systems to be designed and controlled based on the numerical algorithms that are most appropriate for simulating each of the length scales of the process.

2. Challenges and requirements

Here the challenges associated with the design and control of multiscale systems are described, which specify the requirements for multiscale systems tools. To make the description of the challenges as concrete as possible, the manufacture of on-chip copper interconnections in electronic devices is used as an illustrative example. In this process, electrodeposition is used to deposit copper on surfaces and in trenches and vias. The product quality of the deposit is a function of nucleation at the atomic scale, surface morphology at the nanoscale, shape evolution at the nano- to micro-length scales, and deposit uniformity over the wafer surface. This electrodeposition process involves phenomena that are simultaneously important over 10 orders of magnitude in time and length scales (Alkire and Verhoff, 1998). According to the International Technology Roadmap for Semiconductors (Sematech, 2003), the manufacture of next-generation interconnects will require design and control of all these length scales.

Fig. 1 is a schematic of the electrodeposition of copper into a trench, in which Cu^{2+} ions in solution diffuse and migrate to the surface in response to a potential applied between the reference and working electrodes. Although the introduction of organic chemical additive cocktails to the solution to produce void-free copper deposits in sub-100 nm trenches is well established, the precise physicochemical mechanisms of the interactions of these additives with the copper surface are not well understood, making it difficult to design new additive cocktails able to produce void-free deposits in smaller features. A challenge in applying systems principles to these and other multiscale systems is that the underlying mechanisms, as well as the thermodynamic and kinetic parameters associated with the steps in these mechanisms, are uncertain. *Multiscale systems tools are needed that can handle uncertain mechanisms, as well as uncertain parameters*.

Another challenge to engineering multiscale systems is that the codes used to simulate these systems are computationally expensive. For example, consider Fig. 2, which is a schematic of a multiscale simulation model for the electrodeposition of copper into trenches. Chemical reactions and the diffusion and migration of species in the solution boundary layer are described by a system of partial differential-algebraic equations, which are typically simulated using finite differences or finite elements. The height of the boundary layer is typically $\sim$ 50 μm and a typical time step for such a code is $\sim$ 1 ms. The nucleation, surface chemistry, and roughness evolution of the trench surface are most accurately simulated using noncontinuum

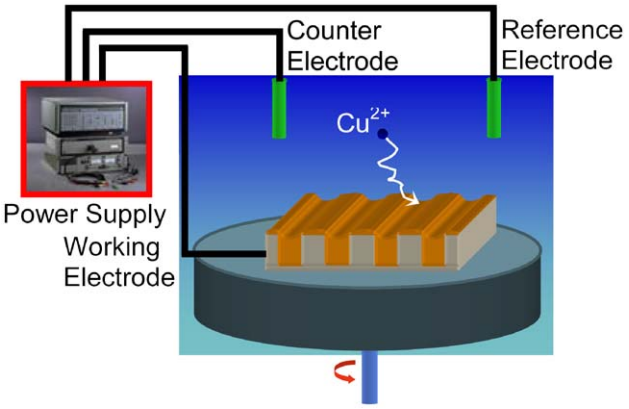

Fig. 1. Electrochemical process for manufacturing on-chip copper interconnects, in which a rotating disk creates a boundary layer above the wafer surface (not drawn to scale).

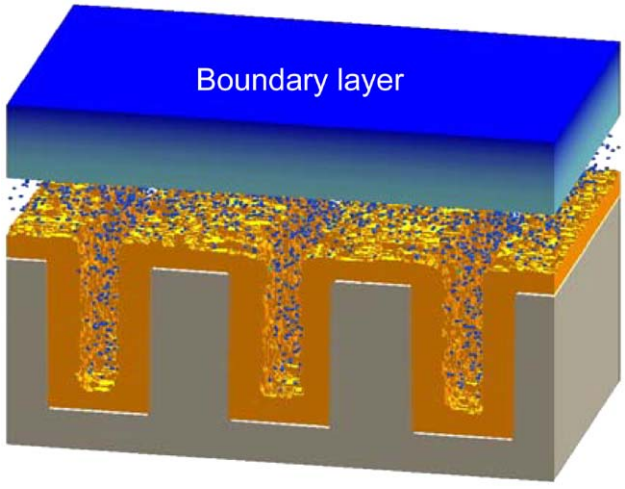

Fig. 2. Multiscale simulation of the electrochemical process for manufacturing on-chip copper interconnects (not drawn to scale).

methods such as kinetic Monte Carlo (KMC) simulation. KMC methods are used to simulate structural properties of matter that cannot be represented by a macroscopic continuum description. A KMC simulation is a realization of the Master equation (Fichthorn and Weinberg, 1991):

$$\frac{\partial P(\sigma,t)}{\partial t} = \sum_{\sigma'} W(\sigma',\sigma)P(\sigma,t) - \sum_{\sigma'} W(\sigma,\sigma')P(\sigma,t), \quad (1)$$

where σ and σ' are successive states of the system, $P(\sigma,t)$ is the probability that the system is in state σ at time t, and $W(\sigma',\sigma)$ is the probability per unit time that the system will undergo a transition from state σ' to σ. For a particular system being studied, the KMC code chooses randomly among the possible transitions of the system and accepts particular transitions with appropriate probabilities. After each accepted or attempted transition, the time variable is

incremented by one Monte Carlo time step (typically the time step is ~ 1 ns), and the process is repeated. By selecting the probabilities to satisfy certain conditions, the real time variable t corresponding to the number of Monte Carlo time steps can be computed.

In Fig. 2 the dynamics within the trench was simulated using a three-dimensional (3D) KMC simulation code, which tracks adsorption, desorption, bulk and surface diffusion, and chemical reactions (Drews et al., 2004). To reduce the computational load, the 3D KMC code was coarse grained, such that groups of molecules were tracked instead of individual molecules (Katsoulaokis et al., 2003), and periodic boundary conditions were used at all sides of the simulation domain. Even with these simplifications, it takes ~ 1 day to perform one simulation run. This greatly limits the number of simulation runs that a systems tool is allowed to make in a coupled simulation-optimization algorithm such as used in control vector parameterization (Ray, 1981). Further, systems techniques that write the simulation code as an algebraic system of equations to be embedded into a structured nonlinear program (Jockenhovel et al., 2003), are not computationally feasible for multiscale systems, as there would be $> 10^{16}$ algebraic equations in the structured nonlinear program. *Multiscale systems tools must be much more computationally efficient than most existing systems tools*. Note that the state dimension of KMC codes is very high, while the numbers of simulation inputs (e.g., applied potential) and outputs (e.g., surface roughness, fraction of voids) are much lower. *This motivates the creation of multiscale systems tools that act directly on simulation inputs and outputs*, to keep the computational cost low.

As a further complication, the codes in Fig. 2 must be dynamically coupled when dilute additives are included in the simulation, as the surface chemistry and transport determines the amount of depletion of additives in the boundary layer, and the boundary layer influences the rate that chemical species reach the surface. *Multiscale systems tools are needed that can handle models described by dynamically coupled continuum and noncontinuum codes*.

A characteristic of noncontinuum codes is that their outputs typically have significant stochastic fluctuations, which can be non-Gaussian. For example, Fig. 3 is the current density response from a dynamically coupled KMC-finite difference simulation of copper electrodeposition in response to a staircase function of the applied potential. The current density only takes on discrete values, which are associated with electron transfer at the copper surface (e.g., Cu^{2+} ion gains two electrons to form copper metal). This response is in sharp contrast to the typical step and staircase responses reported in the controls literature (Ray, 1981). Although most existing systems tools are applicable to stochastic models with Gaussian fluctuations, these tools always assume that the deterministic part of the model is known. *Multiscale systems tools must be able to address models with large amounts of non-Gaussian noise, for which a deterministic model is unavailable*.

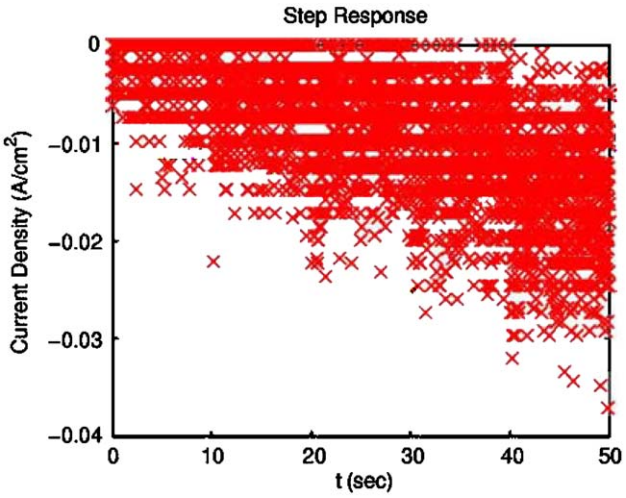

Fig. 3. Current density response to a staircase function of applied potential for the dynamically coupled simulation of the electrochemical process for manufacturing on-chip copper interconnects (each step of the staircase was 10 s long).

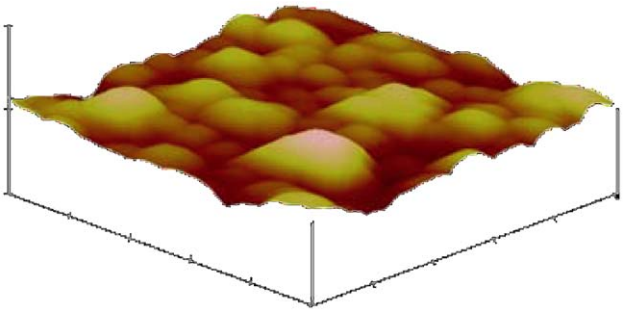

Fig. 4. Atomic force microscopy image of an electrodeposited copper surface.

Another challenge in multiscale systems is the lack of key measurements during processing at industrially relevant operating conditions. For example, the only on-line measured variables for the copper electrodeposition process are temperature and current. There are no concentration measurements at the surface, where the uncertain chemical mechanisms and most of the uncertain parameters are located. The key measurement data, which are atomic force microscopy images, are only available at the end of the process (see Fig. 4). *Multiscale systems tools must include experimental design methods that maximize the information from sensors, to create models that are predictive*.

Another characteristic of multiscale systems is a lack of manipulated variables at the molecular and nanoscopic length scales during processing. For example, the only variable manipulated during the electrodeposition process in Fig. 1 is the applied potential, which is not enough degrees of freedom to produce void-free copper in the 0.13 μm trenches used in modern microelectronic devices. Industrial practice is to introduce additional degrees of freedom in the

initial conditions, which is done through the selection and concentrations of organic chemicals added to the solution. In general, *most multiscale systems require that molecular and nanoscate manipulation be treated as a design focus, to exploit self-assembly during processing*.

3. Systems tools for continuum models

Before looking at multiscale systems tools, it is useful to review some systems tools developed for continuum models that address most, but not all, of the challenges of multiscale systems (see Fig. 5). The first step is the identification of a model, which is an iterative procedure. The first experiment is designed using engineering judgment on how to excite the dynamics of the system, or is computed using initial estimates of the model parameters and some experimental design objective such as minimizing the uncertainties in the parameters. Improved estimates of the parameters and an associated uncertainty description can be computed from the dynamic data collected from the experiment and from ab initio computational chemistry (such as density functional theory) calculations, using Bayesian parameter estimation techniques (Gunawan et al., 2003). When several hypothesized physicochemical mechanisms are available, model selection techniques are used to select which mechanism is most consistent with the experimental data. The model parameters and uncertainty description are used to design the next laboratory experiment, which can be constructed to further reduce the model uncertainties or to maximize the ability to distinguish among the multiple hypothesized mechanisms. Parameter estimates obtained from this iterative procedure can be many orders-of-magnitude more accurate than estimates obtained from data collected from trial-and-error experimentation. Once the model parameters are accurate enough, the simulation model is incorporated into an optimization algorithm to compute the physical design variables, initial conditions, startup procedures, setpoint trajectories, and the feedback control system.

These systems tools are well established for continuum models described by general integro-partial differential algebraic equations (IPDAEs), and have been applied to the manufacture of photographic chemicals (Matthews and Rawlings, 1998), pharmaceuticals (Braatz, 2002), and semiconductors (Gunawan et al., 2004). The key to the generality of these tools is that they act directly on the inputs and outputs of simulation codes, rather than requiring a particular form for the equations or the numerical algorithm used to simulate the equations. The numerical algorithms implemented in the steps in Fig. 5 incorporate parameter sensitivity methods based on finite differences or automatic differentiation (Feehery et al., 1997; Li et al., 2000). The parameter sensitivities improve the numerical conditioning of the systems tools while focusing the modelling effort towards only the key parameters whose values must be known with high certainty to produce predictive models.

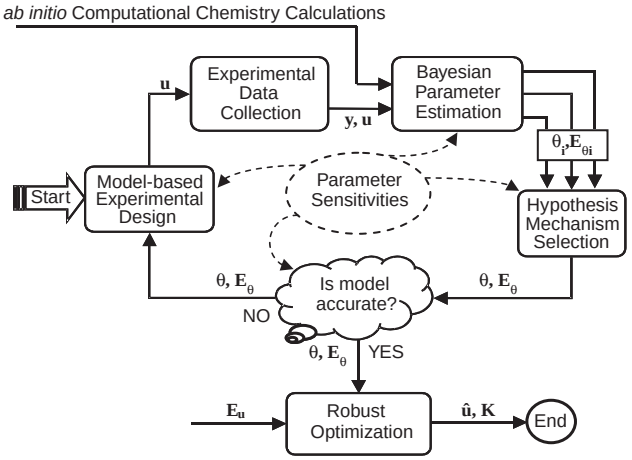

Fig. 5. Iterative process of model identification and robust optimization: **u** represents all experimental design variables (e.g., initial conditions, processing conditions, actuator and sensor locations), **y** represents the measurements, $\boldsymbol{\theta}_i$ is the vector of model parameter estimates and $\mathbf{E}_{\boldsymbol{\theta}i}$ is the confidence region for the *i*th hypothesized mechanism, $\boldsymbol{\theta}$ is the vector of parameter estimates and $\mathbf{E}_{\boldsymbol{\theta}}$ is the confidence region for the most likely mechanism, $\hat{\mathbf{u}}$ is the optimal control policy (including initial conditions, equipment specifications, operating conditions, actuator and sensor locations, etc.), **K** is the optimal controller, and $\mathbf{E}_{\mathbf{u}}$ is the uncertainty in the implementation of the optimal control policy, including the effects of disturbances.

This is especially important when the number of parameters is large, as is typical for microelectronics processes (Gunawan et al., 2003).

In recent years fast techniques have been developed to quantify the effects of model uncertainties on all states and outputs for batch and semibatch processes, and to integrate robustness into all design variables. Some of these techniques have little or no restrictions on the zero dynamics, the integro-differential structure of the equations, the simulation algorithms, or the form of the uncertainties (Pan et al., 1998; Nagy and Braatz, 2003b). These analysis algorithms have been incorporated into optimization algorithms to produce designs and controllers that are robust to the uncertainties (Nagy and Braatz, 2003a).

These systems tools address most of the requirements for application to multiscale systems, in that non-Gaussian stochastic behavior and uncertain mechanisms and parameters are taken into account; the tools are computationally efficient, general purpose, and act directly on simulation inputs and outputs; experimental design methods are included that maximize the information from sensors to create predictive models; and that design and control are optimized simultaneously, which enables molecular and nanoscale manipulation in the design problem to be considered jointly with the manipulation of the on-line variables by feedback controllers during processing. These systems tools do not consider all of the issues particular to models described by noncontinuum and coupled continuum and noncontinuum simulation codes, namely, the lack of an underlying deterministic model for the noncontinuum simulation codes, and additional

numerical stability issues that can arise when codes are linked. The next section discusses some initial steps to extend these systems tools to address these two additional requirements of multiscale systems.

4. Noncontinuum and coupled continuum/noncontinuum codes

For noncontinuum models, the optimizations that occur in the model-based experimental design, Bayesian parameter estimation, hypothesis mechanism selection, and optimal design and control steps in Fig. 5 are stochastic with no closed form expression for the underlying deterministic system, which implies that averaging techniques (Rusli et al., 2003) or stochastic simulation algorithms such as simulated annealing or genetic algorithms are appropriate (Aarts and Korst, 1989). Such approaches are in contrast to the use of reduced-order lattices (Lou and Christofides, 2003), which *increase* the noise level of the simulations. We have shown that even the finite difference calculation of parameter sensitivities typically used in systems engineering algorithms must be formulated as a stochastic optimization problem, to obtain parameter sensitivity estimates of the highest accuracy (Drews et al., 2003a). More specifically, the finite difference expressions for sensitivities reported in textbooks and papers are derived assuming that the underlying system can be described as a deterministic Taylor series expansion, whereas this assumption is invalid for simulations that include noncontinuum models, whose outputs are stochastic. A much more accurate and appropriate formulation is to include a stochastic term in the series expansion, and determine the finite difference expression by solving an optimization problem whose objective is to compute either the minimum variance or maximum likelihood estimate of the parameter sensitivity. As in continuum models, these parameter sensitivities are a key step needed to reduce the computational expense and improve the numerical conditioning of the stochastic optimizations that define the systems tasks in Fig. 5.

Recently we incorporated the stochastic parameter sensitivity algorithm into a multistep optimization algorithm (Raimondeau et al., 2003), that uses sensitivity analysis to determine the key parameters, followed by solution mapping to parameterize the responses of the simulation model as low-degree polynomials of the key parameters, and simulated annealing to optimize the key parameters. This revised algorithm has been used to estimate kinetic parameters associated with copper electrodeposition from measurements of the applied potential and the surface using atomic force microscopy images (see Fig. 4), where the simulation model consisted of a coarse-grained KMC code dynamically coupled to a finite difference continuum code (Drews et al., 2003b).

Further, coupled continuum-noncontinuum codes induce an additional systems issue—linkage instabilities (Raimondeau and Vlachos, 2002). While numerically stable codes are available for simulating each length scale, numerical instabilities can be induced in the linkage of such codes by temporal or spatial mismatches at the interfaces between the codes. Control systems principles can be used to design conditioners on the dynamic information transfer between the simulation codes so that linkage instabilities are suppressed, while self-consistency is maintained (Drews et al., 2004).

5. Summary

This paper delineated the requirements for multiscale systems tools posed by the characteristics of multiscale systems, using the manufacture of on-chip copper interconnections as a specific example to illustrate the key points. Systems tools applicable to continuum models were summarized that satisfy the requirements for multi-scale systems, except for issues specific to dealing with noncontinuum and coupled continuum-noncontinuum codes. Extensions of these systems tools to deal with the requirements of multiscale systems were described, which incorporated stochastic sensitivity analysis within multistep optimization algorithms.

Although the systems principles are the same for multiscale systems as for macroscopic systems, the problem formulations and the numerical algorithms designed to solve these formulations are different. Further, a new issue arises in multiscale systems, which is how to address numerical instabilities that can arise during the linkage of individual simulation codes. Although advances have been made in the analysis of noncontinuum codes (e.g., Gallivan et al., 2001; Makeev et al., 2002), much more research remains to be done. More theory is needed to provide a systematic methodology for the numerical stabilization of multiscale simulation codes, and on algorithms for Bayesian parameter estimation, model-based experimental design, hypothesis mechanism selection, and robust optimization.

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