



# A multiscale systems approach to microelectronic processes

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## Abstract

This paper describes applications of molecular simulation to microelectronics processes and the subsequent development of techniques for multiscale simulation and multiscale systems engineering. The progression of the applications of simulation in the semiconductor industry from macroscopic to molecular to multiscale is reviewed. Multiscale systems are presented as an approach that incorporates molecular and multiscale simulation to design processes that control events at the molecular scale while simultaneously optimizing all length scales from the molecular to the macroscopic. It is discussed how design and control problems in microelectronics and nanotechnology, including the targeted design of processes and products at the molecular scale, can be addressed using the multiscale systems tools. This provides a framework for addressing the “grand challenge” of nanotechnology: how to move nanoscale science and technology from art to an engineering discipline.

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## 1. Introduction

The main objective of this paper is to discuss recent developments in molecular simulation, multiscale simulation, and multiscale systems engineering, and how these developments enable the targeted design of processes and products at the molecular scale. The control of events at the molecular scale is critical to product quality in many new applications in medicine, computers, and manufacturing. These applications include nanobiological devices, micromachines, nanoelectronic devices, and protein microarrays and chips (Alkire & Braatz, 2004; Drexler, 1992; Hoummady & Fujita, 1999; Khanna, 2004; Lee, Lee, & Jung, 2003; Nakano et al., 2001; Prokop, 2001; Sematech, 2004; Tsukagoshi et al., 2002). On the other hand, for efficient operations the manipulated variables available for real-time feedback control operate at macroscopic length scales (for example, the power to heat lamps above a wafer, the fractional opening of valves on flows into and out of a chemical reactor, the applied potential across electrodes in an electrochemical process, etc.). This combination of a need for product quality at the molecular

scale with the economic necessity that feedback control systems utilize macroscopic manipulated variables motivates the creation of methods for the simulation, design, and control of *multiscale systems*.

Nowhere has the trend towards multiscale systems been more evident than in the microelectronics field, where multiscale simulation has been applied for nearly a decade (e.g., see Cavallotti, Nemirovskaya, & Jensen, 2003; Dollet, 2004; Drews, Braatz, & Alkire, 2004; Drews et al., 2005; Jensen, Rodgers, & Venkataramani, 1998; Maroudas, 2000; Nakano et al., 2001; Nieminen, 2002; Rodgers & Jensen, 1998; and citations therein). Subsequent efforts developed techniques for utilizing multiscale simulation models to perform systems engineering tasks, such as parameter estimation, optimization, and control (e.g., see reviews by Braatz et al., 2006 and Vlachos, 2005, as well the papers in this journal issue). This incorporation of models that couple molecular through macroscopic length scales within systems engineering tools enables a systematic approach to the simultaneous optimization of all of the length scales of the process.

Although many of the trends discussed in this paper have counterparts in other applications areas, the focus here is on microelectronic processes because of the many applications of molecular and multiscale simulation to these processes. A

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review of the progression of simulation for the design of micro-electronic processes, including the increased importance of molecular and multiscale simulation, is followed by a discussion of the systems issues that arise when investigating multiscale systems and efforts to address these issues. The paper ends with a discussion of future directions in multiscale systems, and conclusions.

## 2. The trend in simulation from macroscopic to molecular length scales

Anyone familiar with the complexity of an integrated circuit knows that its design and manufacture would be impossible without the extensive application of simulation. In the semiconductor industry the simulation of carrier transport in electronic devices is referred to as *device simulation* and of the processing steps used to manufacture these devices is referred to as *process simulation*. Most of the early simulation codes for both device and process simulation were based on the simultaneous solution of conservation equations written as partial differential-algebraic (PDAE) equations. Device simulation was necessary for the design of transistors in the 1960s (Gummel, 1964; Lee, Lomax, & Haddad, 1974; Scharfetter & Gummel, 1969), when the semiconductor industry was just starting, whereas simulation was applied to many microelectronics manufacturing processes in the 1980s (Barnes, Colter, & Elta, 1987; Graves, 1987; Graves & Jensen, 1986; Park & Economou, 1990; Thompson & Sawin, 1986).

Process and device simulation becomes more challenging as physical dimensions shrink. This trend towards smaller length scales is well illustrated by the well-known Law by Intel co-founder Gordon E. Moore (1965), who noted that the number of transistors per chip had doubled every year since the integrated circuit was invented, and predicted that the trend would continue into the future. This pace of innovation somewhat slowed in subsequent years (see Fig. 1), which resulted in several proposed variations on Moore's Law, the most popular being that the number of transistors per chip doubles every 18–24 months. The

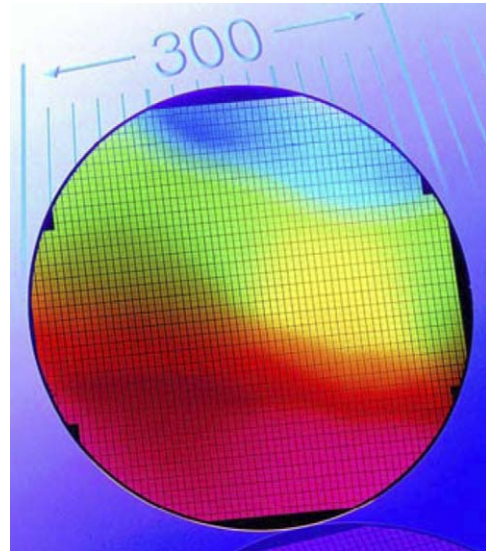


Fig. 2. Integrated circuits on a 300-mm wafer (courtesy of Intel).

International Technology Roadmap for Semiconductors indicates that Moore's Law has a good chance of holding for at least another decade (Sematech, 2004). Following Moore's Law necessitates packing more transistors into smaller dimensions, which has required shrinking the physical dimensions of features in electronic devices from micrometers to nanometers, with molecular dimensions under active investigation (Sematech, 2004).

To gain some appreciation for these length scales, integrated circuits on a 300-mm wafer are shown in Fig. 2. The semiconductor industry often reports a technology generation in terms of a *nominal feature size*, which is the minimum width of a metal wire on the transistor (see Fig. 3). The nominal feature size has been reduced by many orders-of-magnitude since 1960, to its current dimension of 90 nm. Many of the physical dimensions of features in a transistor are actually much smaller than the nominal feature size (see Table 1), and the spatial dimensions

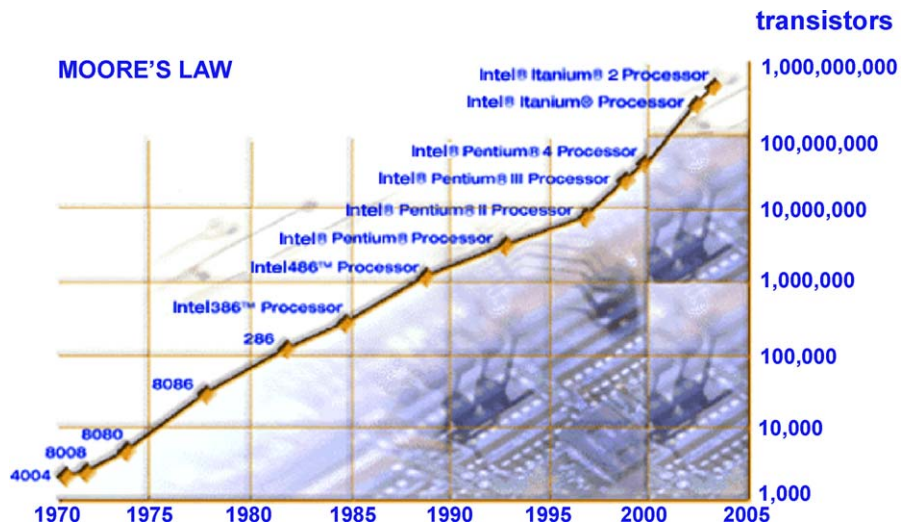


Fig. 1. Moore's Law represented in terms of the number of transistors in an Intel processor (courtesy of Intel).

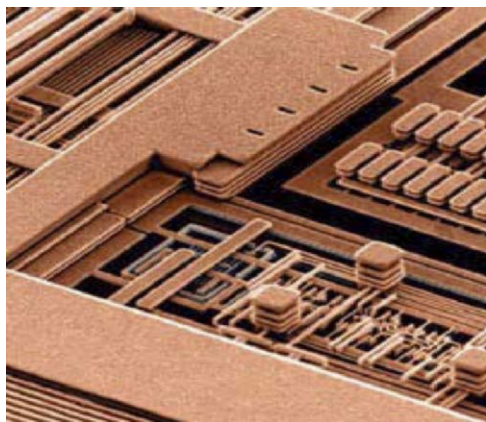


Fig. 3. Copper interconnect structures in an electronic device in which all materials other than copper were etched away, to focus attention on the copper films and wires (courtesy of IBM).

Table 1  
Some physical dimensions of features in a high-volume microprocessor in 2005 (Tables 1g, 47a, and 81a; Sematech, 2004)

Feature	Length (nm)
Nominal feature size	90
Physical gate length	32
Barrier thickness for copper wiring	9
Physical gate oxide thickness	1.1

required to simulate the formation of these features is two orders-of-magnitude smaller. For example, consider the schematic of a metal-oxide semiconductor field-effect transistor (MOSFET) in Fig. 4, which is a common type of transistor. The thin layer of oxide acts as an insulator to separate the channel from the gate. Applying a gate voltage causes the semiconductor in the channel to switch behavior from that of an insulator to a conductor, so that electrons flow from the source to the drain (the source and the drain are typically constructed from copper metal, see Fig. 3). The regions below the source and drain consist of doped silicon, with the *junction* defined as the interface between each doped silicon region and the silicon material below it. A junction depth in a modern MOSFET is typically  $\sim 28$  nm (see Fig. 4). Simulation of the rapid thermal annealing process used to manufacture these junctions requires at least 100 grid cells, resulting a grid cell length of  $28/100$  nm = 0.28 nm, which is the diameter of a silicon atom! Of course under such situations the contin-

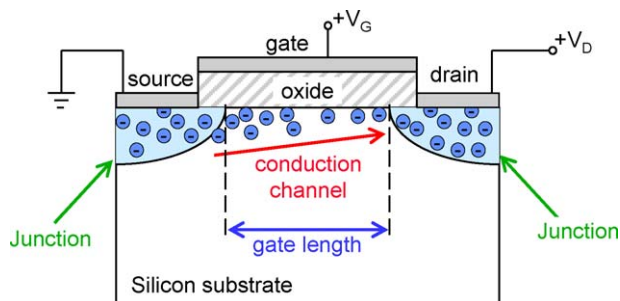


Fig. 4. Schematic of a metal-oxide-semiconductor field-effect transistor (courtesy of Umberto Ravaioli, University of Illinois at Urbana-Champaign).

uum assumption breaks down, which motivates the modeling of this process using atomistic simulation (e.g., the DADOS Monte Carlo simulation package, Martin-Bragado et al., 2004; Pinacho et al., 2004; Rubio et al., 2004).

While most modern simulators for process and device simulation are still based on PDAE models (Grasser & Selberherr, 2002; Kim, McMurray, Williams, & Slinkman, 1998; Pardhanani & Carey, 2000; Rafferty & Smith, 2000; Sibaja-Hernandez, Xu, Decoutere, & Maes, 2005), a purely PDAE representation becomes less applicable as physical dimensions shrink, which has resulted in Monte Carlo simulation becoming important, either as a substitute or as an augmentation to solving PDAE models (Cahill et al., 2003; Grasser, Tang, Kosina, & Selberherr, 2003; Kushner, 1985; Ravaioli, 1998; Saraniti, Tang, Goodnick, & Wigger, 2003; Schoenmaker & Vankemmel, 1992; Sommerer & Kushner, 1992). Molecular simulation has been applied to the chemical vapor deposition of gallium arsenide, which is used in optoelectronics and certain high-speed integrated circuits (Cavallotti et al., 2003; Jensen et al., 1998), the electrodeposition of copper to form interconnects (Drews et al., 2004, 2005), and reactive ion etching, TiN sputtering, and tungsten chemical vapor deposition to form contacts to connect transistor electrodes to wires (Takagi, Onoue, Iyanagi, Nishitani, & Shinmura, 2005). For some device components quantum effects have become important, in which case quantum mechanical calculations must be incorporated (Lake, Klimeck, Bowen, & Jovanovic, 1997; Sano, Hiroki, & Matsuzawa, 2002; Vasileska & Goodnick, 2002).

Most molecular simulation techniques can be categorized as being among three main types: (1) quantum mechanics, (2) molecular dynamics, and (3) kinetic Monte Carlo (KMC) simulation. Quantum mechanics methods, which include *ab initio*, semi-empirical, and density functional techniques, are useful for understanding chemical mechanisms and estimating chemical kinetic parameters for gas phase and solid-state systems (Dalpian, Janotti, Fazio, & da Silva, 1999; La Magna, Alippi, Colombo, & Strobel, 2003). Density functional theory has been very heavily used to compute energy barriers in both diffusion and chemical reactions (Jeong, Lee, Oh, & Chang, 1998; Lin, Kirichenko, Banerjee, & Hwang, 2004; Tuttle, McMahon, & Hess, 2000). The potential energy surface computed by quantum mechanics can be incorporated into molecular dynamics methods, which solve Newton's equations of motion for large numbers of molecules to compute their velocities and positions over time. The forces in Newton's equation ( $F = ma$ ) can be the strong forces due to bonds between atoms and/or weaker forces such as van der Waals or electrostatic forces. Molecular dynamics methods have been used to construct mechanisms and compute diffusion coefficients for many semiconductor processes (Catellani, Cicero, Righi, & Pignedoli, 2005; Goto, Shimojo, Munejiri, & Hoshino, 2004; Ko, Jain, & Chelikowsky, 2002; La Magna et al., 2003; Lee, Lee, & Scheffler, 2004).

A typical molecular dynamics simulation may involve up to a million atoms and simulate a time period of several nanoseconds with time steps of femtoseconds ( $10^{-15}$  s), which is shorter than the time scales associated with most micro- and nanostructure formation. By restricting the *configuration* or *state* of the

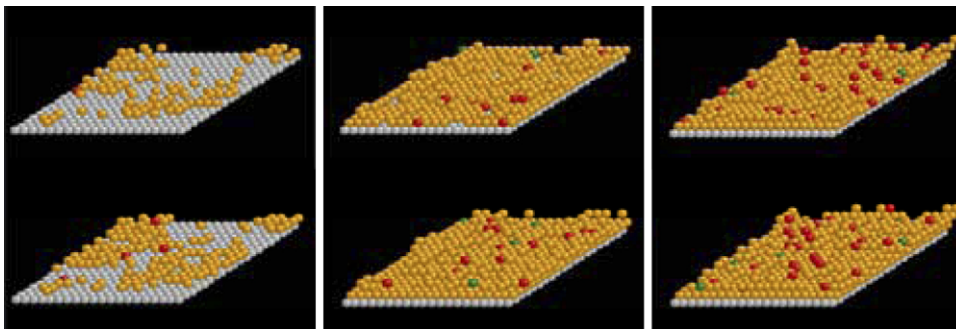


Fig. 5. Six configurations computed during the KMC simulation of the electrodeposition of copper on a substrate (grey spheres) in the presence of additives (red and green spheres) to form a copper film  $\sim 2$ –3 atoms thick.

process to the identity and positions of atoms and/or molecules (see Fig. 5), KMC methods can simulate structural properties of matter that cannot be represented by a continuum description while being able to simulate for much longer times (hundreds of seconds) than can be achieved using molecular dynamics. The chemical mechanism, energy barriers, and diffusion coefficients in the KMC simulation can be obtained from molecular dynamics and quantum mechanics calculations (Nieminen, 2002). The KMC simulation is inherently stochastic, which is consistent with the reality of molecular motion. Due to the large number of degrees of freedom and the stochastic nature of molecular motion, the real process will follow a different state trajectory and arrive at a different state/configuration, each time an experiment is run. Similarly, the configuration resulting from a KMC simulation will be different nearly each time a KMC simulation is run. The probability per unit time,  $W(\sigma, \sigma')$ , that the process will undergo a transition from state  $\sigma$  to  $\sigma'$  can be computed uniquely from the kinetic rates for the individual kinetic steps that can occur in the system (see Fig. 6).

The probability distribution for each configuration is described by the Master equation (Fichthorn & 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  $P(\sigma, t)$  is the probability that the system is in state  $\sigma$  at time  $t$ . This is the conservation equation for the probability distribution for each configuration (accumulation = in – out), with the overall system described by writing Eq. (1) for every possible state/configuration of the system. Because the number of

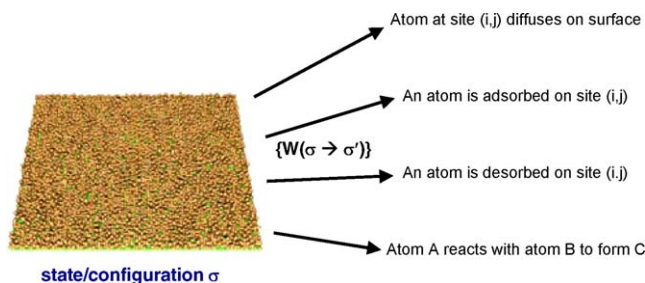


Fig. 6. The set of transition probabilities from a specific configuration  $\sigma$  to a large number of alternative configurations  $\sigma'$  involving a single reaction step (surface diffusion, adsorption, desorption, surface reaction) during the KMC simulation of the electrodeposition of copper.

possible states/configurations is too high to solve these state equations directly, KMC simulation follows a single realization of the Master equation by calling a random number generator to select among the possible transitions with probabilities defined by the kinetic rate laws for each allowed kinetic event (e.g., molecule A moves from one lattice site to the adjoining lattice site, molecule A reacts with adjacent molecule B to form molecule C, etc.). At most one kinetic step can be taken during each time step of the KMC algorithm, with the time step (typically on the order of 1 ns) selected so that the time simulated in the KMC algorithm corresponds to real time (Fichthorn & Weinberg, 1991). Although KMC simulation is much faster than exactly solving the Master equation (Eq. (1)) for each possible configuration, an efficiently implemented KMC simulation for a process of industrial importance (e.g.,  $100 \times 100$  lattice with  $10^{11}$  time steps) typically takes on the order of a day to run.

### 3. The trend towards multiscale simulation and the relationship with nanotechnology

Beyond its increased focus on molecular simulations, the semiconductor industry has been moving towards the integration of simulation domains. For example, the following quotations are from the International Technology Roadmap for Semiconductors (Sematech, 2004), which describes the detailed technology requirements for semiconductor devices for the next 15 years, written by hundreds of company representatives from the semiconductor industry associations of the United States, Europe, Taiwan, Japan, and Korea:

- “The most important trend . . . is the ever increasing need for improving integration between the various areas of simulation.”
- “Different effects which could in the past be simulated separately will in future need to be treated simultaneously . . .”

One of the most difficult challenges in modeling and simulation for the semiconductor industry is reported as being the “integrated modeling of equipment, materials, feature scale processes, and influences on devices” (Table 121 of Asada et al., 2004). This trend of the semiconductor industry towards multi-scale simulation began to be explored a decade ago, and has been an active area of research (e.g., see Cavallotti et al., 2003; Dollet,

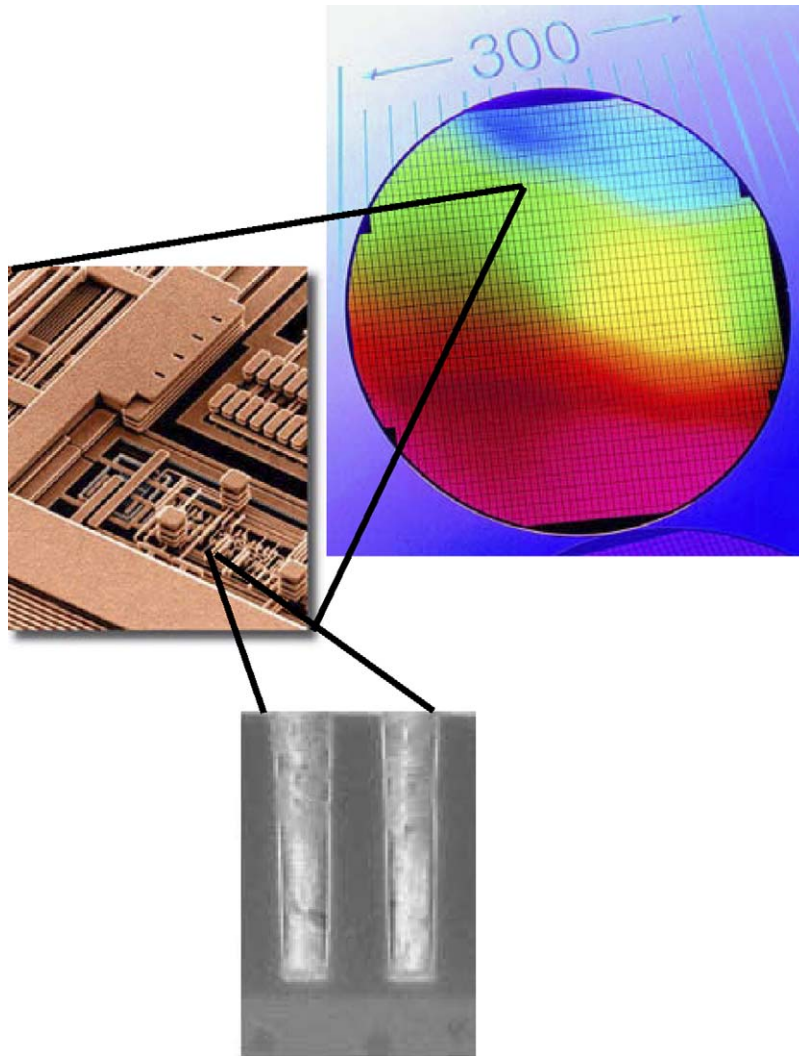


Fig. 7. Integrated circuits in a 30-cm wafer (top right), a portion of the copper interconnect structure within a single integrated circuit with all other material etching away for illustration purposes (left), and the cross-section of two parallel copper wires of  $\sim 90$  nm in width (bottom).

2004; Drews et al., 2004, 2005; Jensen et al., 1998; Maroudas, 2000; Nakano et al., 2001; Nieminen, 2002; Rodgers & Jensen, 1998; and citations therein). As an illustrative example of the multiple length scales involved in a microelectronics manufacturing process, consider the electrodeposition of copper (see Fig. 7). To be profitable, the integrated circuits are simultaneously manufactured on a 300-mm wafer, so each manufacturing process including the copper electrodeposition process requires spatial uniformity over the 30 cm across the wafer. On the other hand, control of length scales  $< 1$  nm are required to achieve uniform filling of trenches to form 90-nm wide copper wires.

The expected future impact of multiscale simulation in the semiconductor industry is suggested by some of the issues associated with the most difficult challenges in modeling and simulation, as stated in the International Technology Roadmap for Semiconductors (Table 121 of Asada et al., 2004):

- “modeling hierarchy from atomistic to continuum for dopants and defects in bulk and at interfaces,”
- “linked equipment/feature scale models,”

- “process modeling tools for the development of novel nanostructure devices (nanowires, carbon nanotubes, quantum dots, molecular electronics),”
- “device modeling tools for analysis of nanoscale device operation.”

While the first two issues are clearly associated with multiscale simulation, the second two issues are associated with nanotechnology and nanoelectronics, which are the future of the semiconductor industry.

The relationship between multiscale simulation and nanotechnology is fairly clear given a coherent definition of nanotechnology. Unfortunately, there are many different definitions of the word “nanotechnology”:

- “the processing of separation, consolidation, and deformation of materials by one atom or one molecule” (Taniguchi, 1996),
- “the ability to work at the atomic, molecular, and supramolecular levels (on a scale of  $\sim 1$ –100 nm) in order to understand, create and use material structures, devices, and systems with

fundamentally new properties and functions resulting from their small structure” (Roco, 2003),

- that which “includes the ability to individually address, control, modify, and fabricate materials, structures, and devices with nanometer precision, and the synthesis of such structures into systems of micro-and macroscopic dimensions such as MEMS-based devices” and “encompasses the understanding of the fundamental physics, chemistry, biology, and technology of nanometer-scale objects and how such objects can be used in the areas of computation, sensors, nanostructured materials, and nano-biotechnology” (Nanotechnology, 2005).

To distinguish between the very broad and very narrow definitions, some researchers have introduced additional terminology, for example, Drexler (1992) defined *molecular manufacturing* as “the construction of objects to complex, atomic specifications using sequences of chemical reactions directed by non-biological molecular machinery” and *molecular nanotechnology* as comprising “molecular manufacturing together with its techniques, its products, and their design and analysis.” These terms contrast with *molecular engineering*, which is typically defined to be the design of a molecule to have desired properties (Ghosh, Grade, & Garcia, 2003; Green & Tidor, 2004; Koberstein, 2004; Larson, 2003; Manstein, 2004).

Rather than debate which “nanotechnology” or “molecular” definitions are the best or most appropriate, the focus here is on techniques for utilizing multiscale simulation models to perform systems engineering tasks, such as parameter estimation, design, and control (Braatz et al., 2006; Vlachos, 2005; and papers in this journal issue). Since multiscale simulation models are capable of directly and simultaneously addressing phenomena across length scales from the sub-atomic to macroscopic, the molecular and nanometer length scales are also covered, and so any systems problems posed for processes at those length scales are just special cases of systems problems defined for multiscale systems. That is, a systems approach that is sufficiently general to handle multiscale systems can also address the problems posed by the various definitions of nanotechnology, molecular manufacturing, molecular nanotechnology, and molecular engineering. The incorporation of models that couple molecular through macroscopic length scales within systems tools enables a systematic approach to the simultaneous optimization of *all* of the length scales, including the optimal control of events at the molecular scale. Such a multiscale systems framework would address the “grand challenge” of nanotechnology: how to move nanoscale science and technology from art to an engineering discipline (Stupp et al., 2002).

The next sections summarize the systems issues characteristic of multiscale systems as well as our views on how to address these issues. The main ideas are illustrated through applications to two processes of importance to the semiconductor industry, one of which involves the successful control of molecular structure and nanometer physical dimensions by the manipulation of sub-atomic phenomena at a gas–liquid interface.

#### 4. Challenges and requirements

Many challenges arise when building models for molecular and multiscale systems:

- uncertainties in physicochemical mechanisms,
- a sparsity of on-line measurements at the molecular scale,
- a sparsity of manipulated variables during processing,
- dynamically coupled model structures and high computational costs for model simulation.

Although quantum mechanics and molecular dynamics calculations can reduce uncertainties in physicochemical mechanisms for some semiconductor processes such as in solid-state systems (Jung, Gunawan, Braatz, & Seebauer, 2004a), these techniques are not sufficiently developed for obtaining accurate results for other microelectronics processes. As an example, consider the electrodeposition of copper to form interconnects (see Fig. 8). In this process  $\text{Cu}^{2+}$  ions in aqueous solution diffuse and migrate to the surface in response to a potential applied between counter- and working electrodes. Many chemical species such as sulfuric acid, copper(II) chloride, polyethylene glycol, mercaptopropanesulfonic acid, and 1-(2-hydroxyethyl)-2-imidazolidinethione must be added to the aqueous solution to produce void-free copper deposits in sub-100 nm trenches (Andricacos, 1999; Andricacos, Uzoh, Dukovic, Horkans, & Deligianni, 1998). Although there is an extensive experimental literature in this area, the detailed chemical interactions of these additives with the copper surface are not well understood (Datta & Landolt, 2000; Kondo, Matsumoto, & Watanabe, 2004; Moffat et al., 2000; Moffat, Wheeler, Huber, & Josell, 2001; Moffat, Wheeler, & Josell, 2004; Tan & Harb, 2003; West, 2000). Examples of questions that must be answered to completely specify a hypothesized mechanism are:

- which chemical species are formed and consumed at the surface?

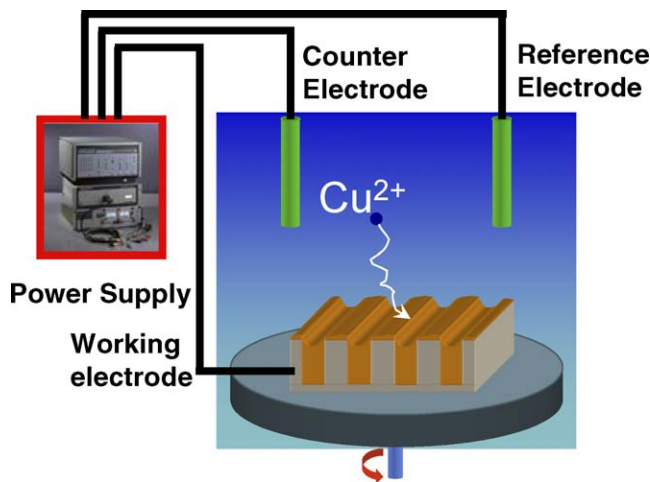


Fig. 8. Electrochemical process for manufacturing on-chip copper interconnects, in which a rotating disk creates a boundary layer above the wafer surface (not drawn to scale).

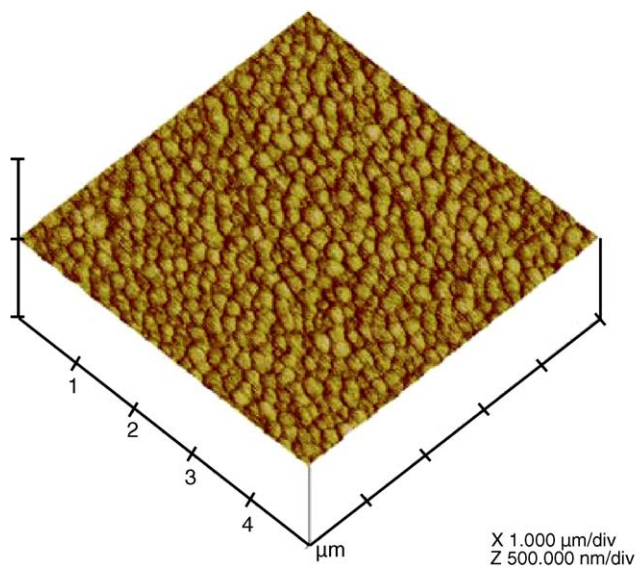


Fig. 9. Atomic force microscopy image of an electrodeposited copper surface ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ).

- what is the physical configuration of each molecule on the surface (e.g., is the molecule sticking out into the solution or flat against the surface)?
- how many sites does each surface molecule cover?

Existing quantum mechanics and molecular dynamics methods have not yet advanced to the stage where water can be reliably modeled by itself (Tu & Laaksonen, 2005; Tuckerman, Marx, & Parrinello, 2002; Wernet et al., 2004; Xenides, Randolph, & Rode, 2005), much less when involved in electrochemical reactions at a surface (Onda et al., 2005). An important requirement of any general multiscale systems framework is that it must be able to enable the resolution of the unknowns in complex heterogeneous mechanisms.

Most molecular systems involve unknown complex heterogeneous chemical mechanisms with no sensors available for measuring concentrations at small length scales ( $<100\ \text{nm}$ ) at industrially relevant operating conditions. For example, the main sensors available for measuring length scales less than  $10\ \mu\text{m}$  for the electrodeposition process in Fig. 8 are scanning electron microscopy and atomic force microscopy (see Fig. 9), which measure surface morphology at the end of the process. Typical sensors measure macroscopic properties such as current, potential, and temperature. *A challenge for such systems is how to construct an accurate chemical mechanism without in-process concentration measurements being available.*

Most processes in which control of events at the molecular scale is important have only 1–2 manipulated variables available during processing. For example, the applied potential is the only manipulated variable during the electrodeposition of copper to form an interconnect (see Fig. 8). A challenge for constructing predictive models for such systems is how to excite the dynamics during model identification experiments when so few manipulated variables are available.

Another challenge when addressing molecular and multiscale systems is that the computational costs for model simulation are

high, and the model structures may require dynamically coupling multiple simulation codes for the various time and length scales (e.g., see Fig. 10). The variety of simulation codes used to model the various time and length scales, as well as the variety of ways in which these codes may be coupled, indicates that systems techniques developed for these systems should be designed to act directly on simulation inputs and outputs rather than being developed for every possible mathematical structure for the model equations. Input-output methods are also motivated by considering that the state dimension for the governing equations implemented in these simulation codes, such as in KMC simulation, can be too high for systems methods to be developed that act directly on the states. The high computational cost also indicates that multiscale systems tools must be very computationally efficient.

## 5. Multiscale systems: addressing the challenges

This section summarizes our views on how to address the challenges posed in the previous section. Substantial unknowns in a complex heterogeneous mechanism can be resolved by estimating the parameters in each hypothesized mechanism and applying existing criteria for model discrimination which select the mechanism that is most consistent with the experimental data (e.g., Burke, Duever, & Penlidis, 1997; Gunawan, Ma, Fujiwara, & Braatz, 2002; Reilly & Blau, 1974; see Fig. 11). The uncertainties in the parameters in each mechanism are quantified by probability distributions that are used to design each subsequent laboratory experiment, either to further reduce the model uncertainties or to maximize the ability to distinguish among the multiple hypothesized mechanisms (Atkinson & Donev, 1992). Parameter estimates determined by quantum chemistry or molecular dynamics calculations can be incorporated using Bayesian estimation, which we have applied to identify the dominant chemical mechanisms during the formation of junctions in metal oxide semiconductor field effect transistors (Gunawan, Jung, Seebauer, & Braatz, 2003).

The questions of how to construct a chemical mechanism without having in-process concentration measurements and how to excite the dynamics during model identification while having few manipulated variables can be addressed by a combination of three methods:

1. design and implement small-scale (e.g., micro- to millimeter scale) chemical systems so as to highly excite the experimental input space,
2. extensively utilize scanning probe measurements,
3. use stop-and-repeat experiments, in which each batch experiment is stopped and analyzed for numerous time intervals to produce dynamic data.

In one application of this approach, we designed and implemented the electrochemical apparatus shown in Fig. 12, in which each experiment deposits copper onto a flat copper substrate with the contact area being a circular disc with diameter of  $\sim 5\ \text{mm}$ . To highly excite the input space, a D-optimal design with 36 experiments was implemented for the wide ranges of

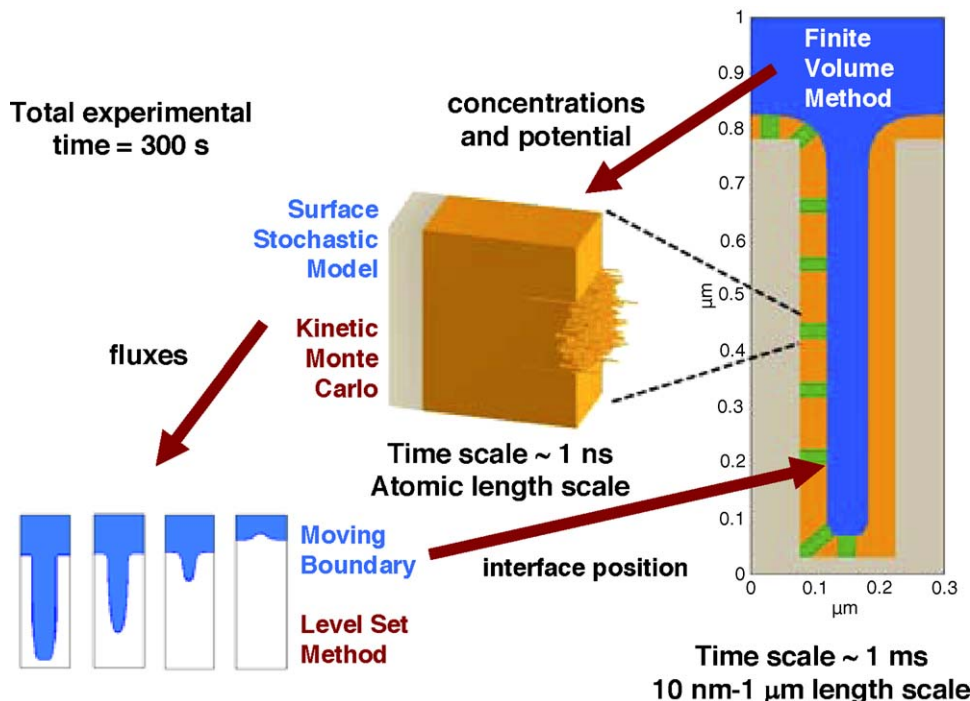


Fig. 10. Schematic of the dynamically coupled multiscale simulation of the electrodeposition of copper into a trench to form a copper wire. A finite volume code which simulates the potential field and concentration fields of all chemical species in aqueous solution sends the solution concentrations and potential at the solid–liquid interface to a KMC code which simulates adsorption, desorption, and chemical and electrochemical reactions that occur on the surface. The KMC code computes fluxes which are sent to a level set code that simulates the movement of the solid–liquid interface and sends its position to the finite volume code for the subsequent iteration. The different time scales are addressed by implementing many events in the KMC code for each time interval of the finite volume code. Higher accuracy can be obtained by iterating all three sets of codes to convergence at each time instance.

input variables shown in Table 2. Although the industrial interest is in depositing within trenches and vias to form copper wires and multilayer contacts, the experiments were designed for deposition on flat surfaces so that surface morphology can be measured by using scanning probe measurements, in this case, atomic force microscopy (see Fig. 9)—greatly expanding the measurements obtained in each experiment.

Each of the experiments in the D-optimal design was repeated two to three times, with each experiment starting with a newly polished wafer. Eight surface locations were measured for each experiment, to characterize both experimental noise and biases. Since the AFM images are only available at the end of each experiment, each experiment was repeated for  $\sim 10$  batch times,

with times selected to capture the dynamics for each experimental condition (e.g., see Fig. 13). The parameters in a KMC code were estimated by applying the methods in Fig. 11 to the potential/current and root-mean-squared surface roughness curves (see Figs. 13 and 14).

One question that arises with such an approach is how well the model parameters associated with surface diffusion and the chemical and electrochemical reactions can be extracted from the current, potential and ex situ surface morphology data, given the complex nature of the interactions of the additives with the surface (e.g., see Table 3). A key point is that current and potential curves and the surface morphology are very sensitive to changes in the experimental inputs (shown in Table 2), indicating that the large quantity of experimental data collected for the wide range of experimental inputs contain substantial information about the underlying mechanism. Further, changes in

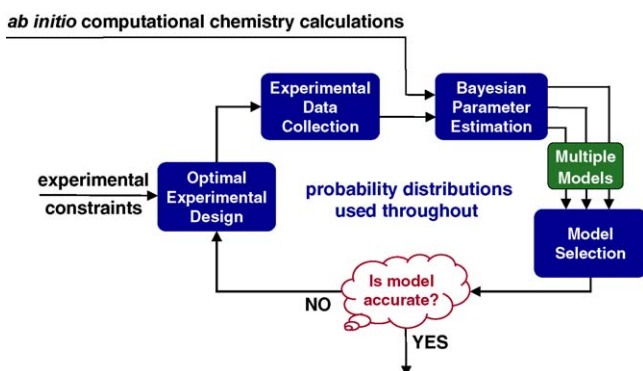


Fig. 11. Model building using Bayesian estimation and model discrimination/selection.

Table 2

Lower bound, centerpoint, and upper bound for the inputs for a set of millimeter-scale electrochemical experiments

Perturbed experimental inputs	Experimental range
CuSO <sub>4</sub> concentration	0.3, 0.7, 0.8 M
H <sup>2</sup> SO <sub>4</sub> concentration	5, 45, 175 g/L
SPS concentration	3, 26.5, 50 ppm
PEG concentration	0.1, 0.3, 3 g/L
Cl <sup>-</sup> concentration	10, 55, 100 ppm
HIT concentration	5, 50, 200 ppb
current density	3, 11.5, 20 mA/cm <sup>2</sup>



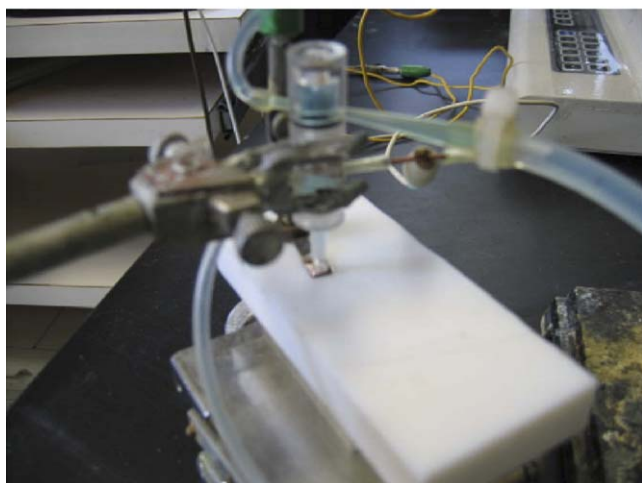
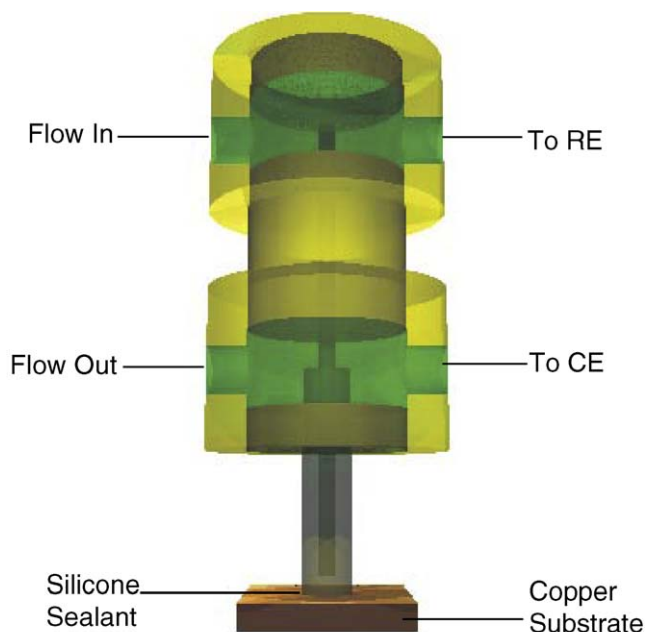


Fig. 12. Millimeter-scale fluidic system used to collect experimental data for constructing models for copper electrodeposition.

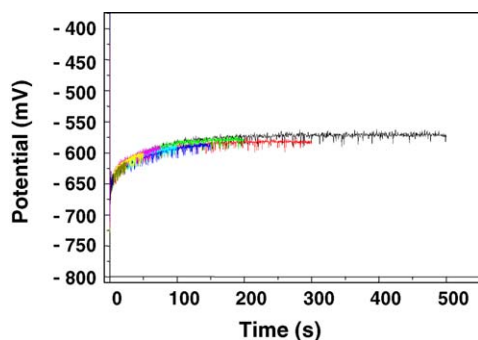


Fig. 13. Applied potential curves for one set of experimental conditions in Table 2 measured for the experimental system shown in Fig. 12. Each color corresponds to a batch with a different batch time.

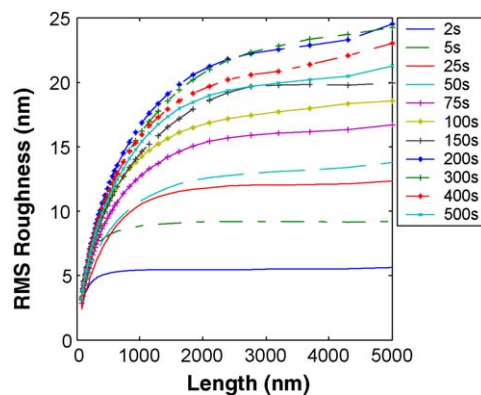


Fig. 14. Root-mean-squared surface roughness as a function of length scale and time, averaged over eight locations, at one set of experimental conditions in Table 2.

Table 3

The hypothesized electrochemical-chemical mechanism for the electrodeposition of copper in the presence of additives resulting from application of the model building approach of Fig. 11

1.	$\text{Cu}^{+2}(\text{aq}) + \text{e}^{-} \rightarrow \text{Cu}^{+}(\text{aq})$
2.	$\text{Cu}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$
3.	$\text{Cu}(\text{s}) \rightarrow \text{Cu}(\text{s})(\text{surface diffusion})$
4.	$\text{Cu}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \rightleftharpoons \text{CuCl}(\text{ads})$
5.	$\text{CuCl}(\text{ads}) + \text{e}^{-} \rightarrow \text{Cu}(\text{s}) + \text{Cl}^{-}(\text{aq})$
6.	$\text{CuCl}(\text{ads}) + \text{PEG}(\text{aq}) \rightleftharpoons \text{Cu(I)-Cl-PEG}(\text{ads})$
7.	$\text{SPS}(\text{aq}) + 2\text{e}^{-} \rightarrow 2\text{thiolate}^{-}(\text{aq})$
8.	$\text{Cu}^{+}(\text{aq}) + \text{MPS}(\text{aq}) \rightleftharpoons \text{Cu(I)thiolate}(\text{ads}) + \text{H}^{+}(\text{aq})$
9.	$\text{Cu(I)thiolate}(\text{ads}) + \text{Cu}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Cu}(\text{s}) + \text{Cu(I)thiolate}(\text{ads})$
10.	$\text{Cu(I)thiolate}(\text{ads}) + \text{HIT}(\text{aq}) \rightarrow \text{Cu(I)HIT}(\text{ads}) + \text{MPS}(\text{aq})$
11.	$\text{Cu(I)HIT}(\text{ads}) + \text{H}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Cu}(\text{s}) + \text{HIT}(\text{aq})$
12.	$\text{thiolate}^{-}(\text{aq}) + \text{H}^{+}(\text{aq}) \rightleftharpoons \text{MPS}(\text{aq})$
13.	$\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}^{+}(\text{aq}) + \text{HSO}_4^{-}(\text{aq})$
14.	$\text{HSO}_4^{-}(\text{aq}) \rightleftharpoons \text{H}^{+}(\text{aq}) + \text{SO}_4^{-2}(\text{aq})$

the hypothesized mechanism or the sensitive model parameters being estimated have a very strong effect on the current, potential, and ex situ surface morphology, which suggests that the data may be sufficient for the model parameters to be identifiable. The chemical-electrochemical mechanism that arose from applying the model building approach of Fig. 11 to the experimental data is shown in Table 3, with the values of the parameters in the most sensitive reactions shown in Table 4. The associated uncertainty analysis indicated that the model parameters were identifiable from the experimental data (readers interested in more details on the parameter estimation and discussion of results are referred to Ph.D. theses by Rusli, 2006 and Xue, 2006).

Table 4

Values of model parameters in the most sensitive reactions in the mechanism, with “(→)” indicating that the sensitive model parameters are only in the forward reaction.

Reactions	$k$	$\alpha$
1	$6.9 \times 10^{-2} \text{ m/s}$	0.20
2(→)	$1.4 \times 10^{-3} \text{ m/s}$	0.51
4(→)	$15 \text{ m}^4/\text{mol s}$	–
6(→)	$100 \text{ m}^4/\text{mol s}$	–
8(→)	$1.4 \times 10^8 \text{ m}^4/\text{mol s}$	–

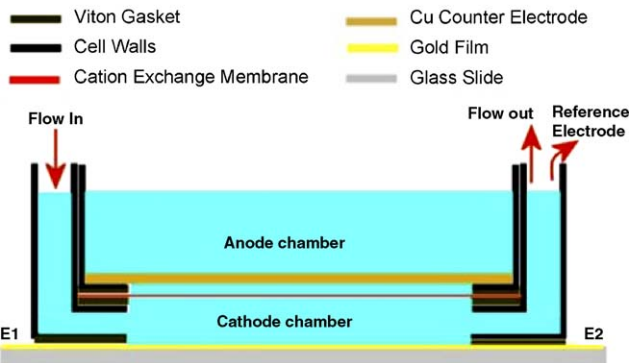
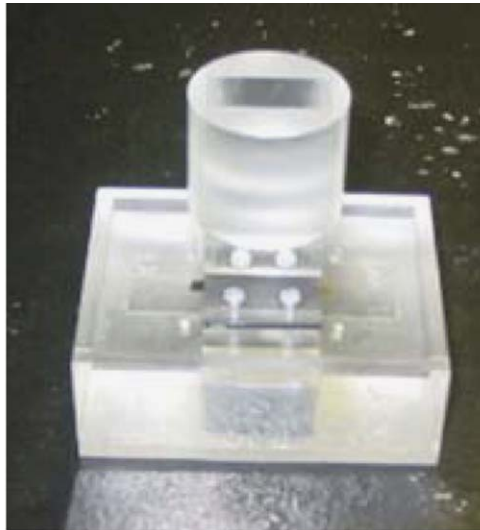


Fig. 15. Electrodeposition of copper on a bipolar gold electrode: electrochemical cell (top) and schematic of cell (bottom).

Recently, we have taken this approach of designing millimeter-scale chemical/electrochemical systems for high-throughput data collection a step further, by designing an apparatus in which the potential varies across the electrode (see Fig. 15). This enables the measurement of the effects of a wide range of potential in a single batch experiment. At the end of each experiment the surface morphology is measured along the electrode by using atomic force microscopy.

The implementation of the systems methods in Fig. 11 is well established for deterministic simulation codes (e.g., see Braatz et al., 2006, and references cited therein), whereas the systems methods for stochastic simulation codes utilize multistep optimization (see Fig. 16). The multistep optimization of Raimondeau, Aghalayam, Mhadeshwar, and Vlachos, 2003 utilizes sensitivity analysis to determine the key parameters, followed by response curve mapping to parameterize the responses of the simulation model as low-degree polynomials of the key parameters, and simulated annealing to optimize over the key parameters. Fig. 16 revises this algorithm to utilize stochastic sensitivities (Drews, Braatz, & Alkire, 2003) and optimal design methods to reduce the computational cost per iteration, and revises the structure of the low-order models, based on any known physics, to improve the quality of the low-order model identified in each iteration (Braatz et al., 2006). Either approach applies to multiscale simulation codes with arbitrary (but well-posed) dynamic coupling of individual simulation codes. [Details on multiscale simulation issues including guidelines for dynamically coupling codes and conditions for well-posedness, numerical convergence, and numerical accuracy are discussed in previous reviews (Braatz et al., 2006; Karulkar, He, Alkire, & Braatz, 2005); this paper focuses on multiscale systems issues.]

Once a model is constructed, it can be used for the optimization of all time and length scales, using a similarly constructed

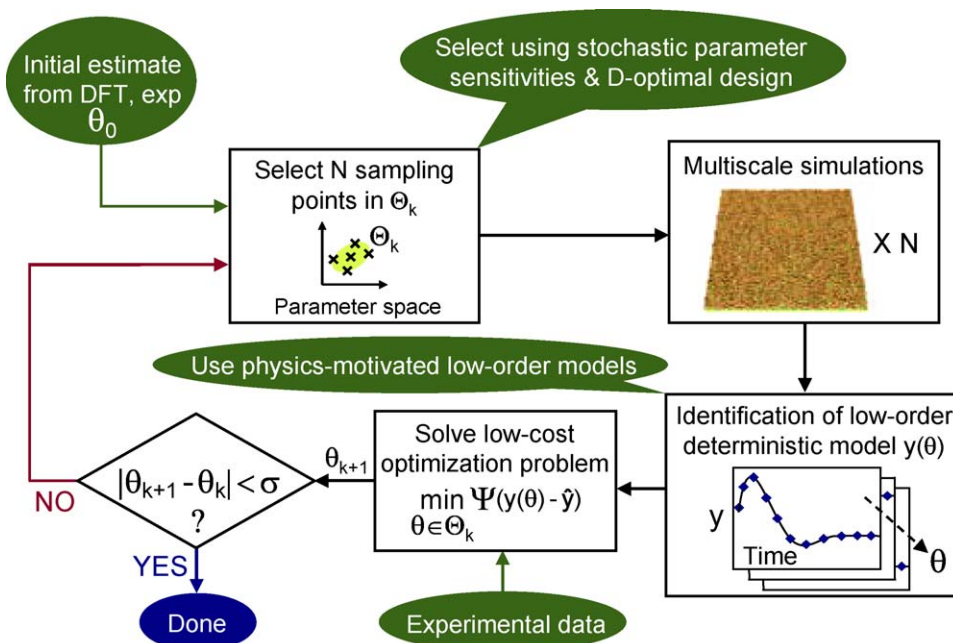


Fig. 16. Multistep optimization for the estimation of parameters in stochastic simulation codes.

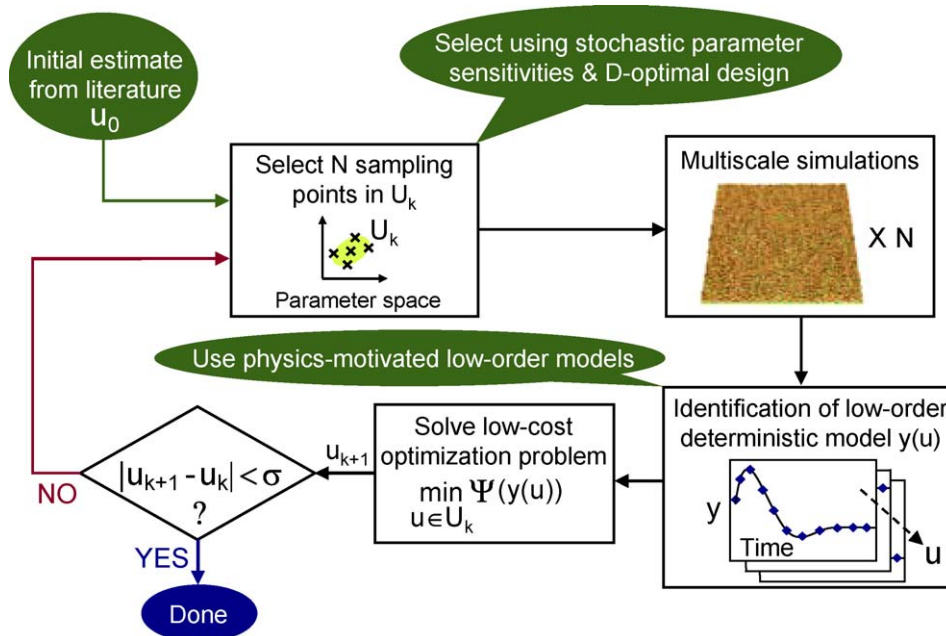


Fig. 17. Multistep optimization for design and control using stochastic simulation codes.

multistep algorithm (see Fig. 17). The multistep algorithms in Figs. 16 and 17 are the same numerically, but with different optimization variables, objectives, and constraints. The optimization objective can be formulated to ensure robustness to the model uncertainties quantified in the parameter estimation procedure (e.g., see Nagy & Braatz, 2003, and citations therein). The optimization variables  $u$  can include operating variables (e.g., batch control trajectories), feedback controller parameters, and parameters that define the molecules in the system (e.g., polymer chain length, hydrophobicity, etc.). This provides a systematic methodology for the control of events at the molecular scale while simultaneously optimizing all length scales from the molecular to the macroscopic. By its inclusivity of other time and length scales, the multiscale systems approach can address the modeling and design problems of nanotechnology, molecular nanotechnology, and molecular manufacturing.

Although the multistep algorithms in Figs. 16 and 17 were designed for use with stochastic simulation codes, these algorithms also can be applied for processes modeled by deterministic simulation codes, in which case the multistep algorithms are similar to successive quadratic programming. We have applied this approach to design a better process for the formation of ultrashallow junctions in metal oxide semiconductor field effect transistors. The process for forming junctions involves ion implantation of dopants into bulk semiconductor followed by rapid thermal annealing (RTA) using high-powered lamps. The RTA step electrically activates the dopant but promotes unwanted dopant diffusion into the bulk. A PDAE model was constructed from Poisson's equation for the electric field and the reaction-diffusion-migration equations which included reactions for the transfer of boron and silicon atoms between interstitial and substitutional positions and for the formation and dissolution of boron, silicon, and mixed boron-silicon clusters. Model selection methods were used to select among compet-

ing chemical mechanisms and to simplify the reaction network (Jung, Kwok, Braatz, & Seebauer, 2005). Activation energies in the mechanism were estimated by the application of Bayesian estimation to density functional theory calculations and isolated experiments in the literature, resulting in agreement of measured boron profiles within  $\sim 1$  nm. The simulation model was validated with extensive literature data which employed various doping energies, doses, and temperature programs (Gunawan et al., 2003). Application of optimization indicated that the existing RTA process in industry was already operating at nearly optimal electrical activation and junction depths (Gunawan, Jung, Seebauer, & Braatz, 2004), which motivated the expansion of the optimization variables to include the bond structure at the silicon surface (Jung, Gunawan, Braatz, & Seebauer, 2004b). We have shown that modifying the structure of bonds at the silicon surface enables precise nanometer-scale control of the junction depth due to a change in the effective surface boundary condition for interstitials. These simulation studies have motivated discrete changes in processing conditions, which are being evaluated experimentally (Kwok, Dev, Braatz, & Seebauer, 2005) and form the basis of a patent application (Seebauer, Braatz, Jung, & Gunawan, 2004).

## 6. Directions for future research

The most important direction for future research is the application of the multiscale systems approach to a broad range of specific problems. The greatest number of applications in the near term is likely to be in micro- and nanoelectronics, given the head-start in applications of multiscale simulation and the intense interest of the semiconductor industry, as cited earlier in this paper. More specific applications are likely to arise in nanobiomedical sensors and other nanobiological devices, many of which are closely related to micro- and nanoelectronic

processes in terms of chemistry, physics, materials, and components. These specific applications will certainly serve also to improve the systems tools, as any nontrivial applications are apt to do.

The multiscale systems tools discussed in the previous section have minimal restrictions on the zero dynamics, the integro-differential structure of the governing equations, the simulation algorithms, or the form of the nonlinearities or uncertainties. The optimization in Fig. 17, however, is only well-developed for finite-time processes, that is, batch and semibatch processes with a limited set of transitions. This is not particularly restrictive for the vast majority of micro- and nanotechnological processes. On the other hand, both infinite-time (referred to as “continuous” in the chemical engineering literature) and finite-time mixed discrete-continuous processes with a large number of transitions pose open theoretical issues. When the optimization is generalized to infinite time, the control theoretical notions of unstable zero dynamics and closed-loop stability become important, and the use of a purely input-output approach may be too limiting. No nonconservative technique is available for the analysis of robustness for nonlinear infinite-time systems, much less the optimization of such systems (while it is trivial to make enough assumptions on the governing equations to derive sufficient conditions for obtaining closed-loop stability, such mathematical exercises are often of no practical utility). When the process is finite time with a large number of potential transitions then the optimization in Fig. 17 can have too many local solutions or be too computationally expensive to be feasible with available computing power. This problem is not completely solved even for models described by deterministic equations such as differential-algebraic equations (Chachuat, Singer, & Barton, 2005), much less the much more challenging case of stochastic simulation.

## 7. Conclusions

This paper reviewed the challenges of multiscale systems, and how these challenges can be addressed by (i) design and implementation of high-throughput millimeter- and micrometer-scale chemical/electrochemical systems so as to highly excite the experimental input space, (ii) extensive utilization of scanning probe measurements, (iii) utilization of stop-and-repeat experiments, (iv) an iterative model building procedure consisting of Bayesian estimation and mechanism selection, and (v) multi-step optimization. It is argued that the multiscale systems approach is directly applicable to problems in nanotechnology, molecular nanotechnology, and molecular manufacturing. The key ideas were illustrated with applications to two processes of importance to the semiconductor industry: the electrodeposition of copper to form interconnects and junction formation in metal oxide semiconductor field effect transistors.

It is argued that the most important direction for future research is the application of the multiscale systems approach to a broad range of specific problems, and that the largest open theoretical problems are in addressing hybrid and infinite-time multiscale systems.

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