Multiscale Modeling of Hard Materials: Challenges and Opportunities for Chemical Engineering

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The basic science and engineering of hard materials, such as those used in electronic and optoelectronic device fabrication, has been an area of increasing interest and activity within the chemical engineering profession. Ameasure of this activity is the growing number of chemical engineers employed in the semiconductor manufacturing industry. Improved and novel engineering of hard materials, including elemental and compound semiconductors, dielectric materials, and metallic thin films, has enabled the development of new technologies that aim to meet worldwide market demands at fast rates. In microelectronics and optoelectronics technologies, global trends for ultra-large-scale integration and miniaturization of devices require precise information regarding materials' properties and microscopic physicochemical mechanisms, detailed description of various processing steps involved in device fabrication, as well as accurate predictions of materials' reliability during device function. To address these needs, materials modeling and computer simulation have emerged as a cost-effective tool for developing materials and process design strategies.

A crucial need in the electronics industry is the establishment of quantitative relationships among materials processing, structure, and function. The role of modeling in addressing this need has been realized recently through important methodological advances and substantial increase in computational power. Materials systems of industrial interest are highly heterogeneous, characterized by a variety of interfaces, defects, and microstructural features. Length scales characteristic of such materials' structural features span a wide range from atomistic to continuum scales. This heterogeneity of materials structure is typically the product of hundreds of processing steps including chemical vapor deposition, plasma etching, and ion implantation. Quantitative prediction of the behavior of heterogeneous materials systems requires fundamental physicochemical knowledge and understanding, as well as both wide transferability and high power of computational machinery in order to integrate various computational methods throughout the range from the atomistic to the continuum scale. The ability to carry out such a task for any material system of technological interest presents both a major challenge and a tremendous opportunity for chemical engineers.

The elements

Figure 1 highlights the *elements* of a multiscale methodological approach capable of addressing the wide range of length and time scales inherent in a heterogeneous material system. Toward both ends of the length/time-scale spectrum, atomistic and continuum, mature and highly sophisticated computational techniques are available for implementation. Computational quantum mechanics within the framework of density-functional theory enables accurate calculations of materials properties, including defect, surface, and interfacial properties (Payne et al., 1992). For such calculations, the typical size of the computational domain (the simulation supercell) is on the order of one nanometer, while the equations of ionic motion are integrated through *ab initio* molecular-dynamics (MD) schemes over times of several picoseconds (Car and Parrinello, 1985; Payne et al., 1992). Sacrificing accuracy in describing interatomic interactions allows for larger simulation cells and longer MD trajectories, pushing the length and time scales up to one hundred nanometers and several nanoseconds, respectively, while retaining the atomistic description of the material system. Such less accurate descriptions are based on semiempirical or empirical expressions of the material's total energy (Hamiltonian); the resulting degree of accuracy depends on the parameterization of the Hamiltonian. At this level of theory, the machinery of computational statistical mechanics, namely molecular-statics, lattice-dynamics, Monte Carlo, and molecular-dynamics simulations (Abraham, 1986; Allen and Tildesley, 1990; Rapaport, 1995), can be used to provide additional physicochemical information over scales that are intractable by direct implementation of computational quantum mechanics. Such atomic-scale simulations are valuable particularly in obtaining fundamental mechanistic understanding of the material's response to external forces. Finally, at the continuum end of the spectrum, the physical law of fundamental conservation principles is expressed by the rigorous mathematical formalism of continuum mechanics and supplemented by constitutive relations and boundary conditions to result in well posed boundary-value problems. These problems are solved numerically in continuous domains that are discretized based on finite-difference, finite-element (Strang and Fix, 1973), or boundary-element methods (Kane, 1993). Such domain discretization techniques enable macroscopic process modeling over length and time scales from inches to reactor scales and time scales from seconds to hours (Maroudas and Shankar, 1996).

Intermediate between atomistic and continuum scales lies a regime termed mesoscopic or microstructural. This is a very important regime to "probe" for modeling heterogeneous materials with fine microstructure. At this scale, the objects of interest are large collections of atoms arranged in the form of, e.g., grains, precipitates, cavities, or interfacial faults; characteristic length scales range from fractions to hundreds of microns. Although this regime is currently "searching" for a rigorous theoretical and methodological identity, computational practitioners have been implementing at this scale techniques borrowed from the atomic or the continuum scale:

such implementations may involve many millions of atoms in an atomistic simulation cell or very fine grids in a continuous domain discretization scheme, or combinations of the two. At every length scale, time-scale multiplicity creates additional problems. Finally, predicting heterogeneous materials behavior requires integration of the above elements into a *nonlinear system* problem that is usually very complex. Consequently, systematic parametric studies are necessary for developing optimal materials processing or materials reliability strategies. Throughout the range of length and time scales, methods of bifurcation and stability analyses (Iooss and Joseph, 1990) can be implemented to assess and optimize the quality of a material process or the performance of a device.

(quantum mechanics). Materials modeling, however, cannot be based exclusively on first principles. In spite of the continuous increase in computational power that will enable *ab initio* calculations over larger length scales and longer time scales, parametric studies at this level of theory will remain impractical. On the other hand, quantitative predictions cannot rely solely on empirical phenomenology: such empiricism is not transferable to widely different materials environments. Finally, regardless of computational capabilities for quantitative predictions, fundamental mechanistic understanding is of utmost practical importance: only such understanding can provide the necessary insights to guide efficiently parametric studies and design of experimental protocols.

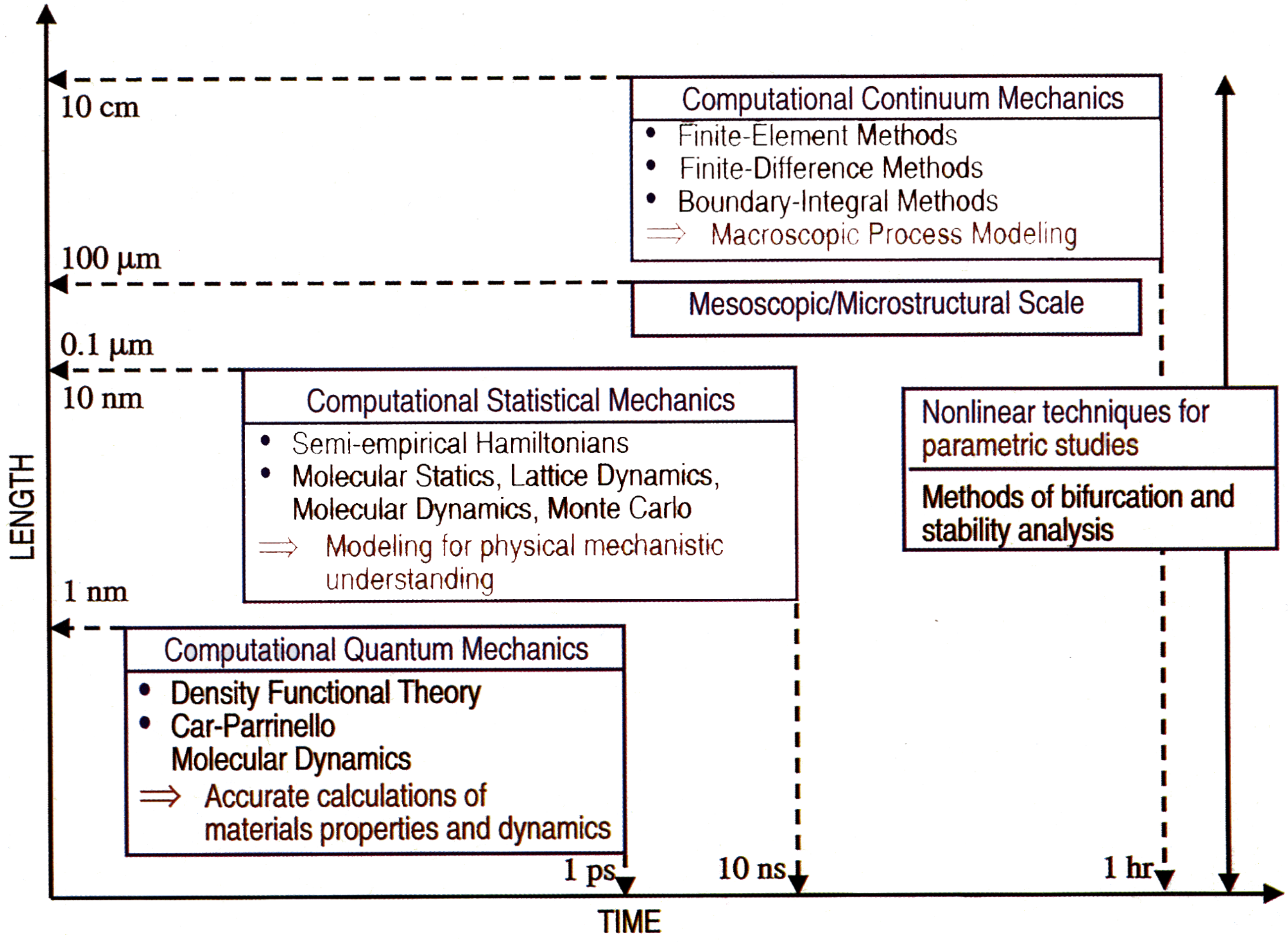

Figure 1. Elements of multiscale methodological approaches for computational materials science and engineering.

Integrating the elements: pathway to technological innovation

Integrating rigorously the elements outlined above is the main goal of multiscale modeling. It is this *integration* that can provide a pathway to improved materials engineering and technological innovation. Modeling for qualitative understanding of physicochemical mechanisms is not sufficient for designing future generations of more powerful, reliable devices; instead, fully predictive modeling capabilities are required. Quantitative accuracy in predicting materials behavior is guaranteed only by connection to first principles

How to integrate the elements: challenges and emerging strategies

Linking widely different space scales has been based on two general modeling strategies: a "parallel" and a "serial" strategy. In the parallel approach, different-scale techniques are implemented simultaneously in the same computational domain that is decomposed appropriately. Important contributions in this category include the quasi-continuum methodology (Tadmor et al., 1996) and the macroscopic-atomistic-*ab initio* dynamics (MAAD)approach to fracture mechanics (Broughton et al., 1999). In the quasi-continuum method, a defective material system is embedded within a continuum represented by an adaptive finite element (FE)mesh that is refined down to atomic dimensions. The system energy is determined by an underlying atomistic Hamiltonian; a separate atomistic structural relaxation calculation is required for each cell of the FE mesh instead of using empirical constitutive information. In the MAAD method, crack propagation in a solid is simulated by coupling a quantum mechanical description within the tight binding approximation with classical molecular dynamics (MD) based on an empirical potential. As one moves to a far-field region away from the tip of the propagating crack, the MDcell is embedded in an FEmesh for computing the displacement field within continuum elasticity theory; the corresponding elastic moduli are computed according to the potential used in the MD. Fully parallel strategies, such as MAAD, are currently limited to systems that involve a central defective region surrounded by a region which is only slightly perturbed from equilibrium; thus, they are not ideally suited for simulating complex material systems. The continuous increase in computing power, however, in conjunction with major recent advances in implementing computational materials science methods in massively parallel computing platforms (see, e.g., Nakano et al., 1999) hold promise for wider future usage of such parallel multiscale strategies.

The serial approach has been used more extensively. In this approach, different-scale techniques are implemented sequentially in different computational domains at different levels of discretization ranging from discrete atoms to continuum material elements; information (output) is passed (as input) from finer to coarser scales. The inherent structural and chemical complexity of materials systems of chemical engineering interest has motivated serial multiscale strategies in establishing relations among materials' microstructure, processing, and reliability (Maroudas and Shankar, 1996). Representative examples of such multiscale modeling include microdefect formation in the bulk melt growth of single crystalline silicon (Sinno and Brown, 1999), thin film growth on semiconductor wafers in chemical vapor deposition reactors (Jensen et al., 1998), and electromechanically-induced failure of metallic thin films used as device interconnections in integrated circuits (Gungor et al., 1999), which is mediated by void growth and morphological evolution (see cover).

Widely varying time scales pose additional severe restrictions to predictive materials modeling, regardless of strategy for linking multiple space scales. In "parallel" length-scale methodologies, for example, the time scale is set by the finest atomic-scale method involved in the multiscale scheme; this is typically up to one nanosecond. Such time-scale limitations can be overcome by dynamical Monte Carlo (MC) methods (see, e.g., Fichthorn and Weinberg, 1991), which allow for stochastic propagation of the dynamical system using time steps coarser by orders of magnitude than those employed typically in MD methods. The coarse time steps are determined, e.g., by the rates of slow diffusional processes through the corresponding thermal activation barriers; these rates are input quantities for the MCsimulation. Such techniques are termed collectively as kinetic Monte Carlo (KMC)and can be implemented on either lattices or disordered media. The main limitation of KMCis that its accuracy depends on the completeness and accuracy of the input database of transition probabilities. A promising alternative to KMC, which is currently at an exploratory stage is the method of "hyperdynamics" for accelerating the MD simulation of infrequent events in solid material systems (Voter, 1997). In this method, the energy in regions other than the transition states between potential basins is raised by a bias potential, thus accelerating the rate of transitions and making the actual elapsed time a statistical property of the system. In analogy with the classification of multispace-scale strategies, KMC and hyperdynamics can be viewed as "serial" and "parallel" approaches, respectively, in the context of time stepping the system trajectory during its evolution.

The opportunity: multiscale modeling for materials system design

Over the past decade, multiscale materials modeling has evolved from a dream to an area of intensive methodological development to a working tool of industrial interest. The tremendous opportunity in the field lies in the capabilities of this tool for designing new materials systems and manufacturing processes. Enabling such design is indeed possible for a large class of technologically interesting systems based on currently available computing power.

These capabilities are highlighted using an example from our own work at UCSB, as summarized in Figure 2. In this case, the modeling goal is to design experimental protocols toward the development of engineering strategies for strain relaxation of semiconductor films grown heteroepitaxially on semiconductor substrates. The origin of strain is the lattice mismatch between the film and substrate materials; controlling this strain, which is a driving force for defect generation, is the key to optimizing the film's optoelectronic properties. The design is based on fundamental understanding and quantitative prediction of the energetics and kinetics of strain relaxation mechanisms, such as defect formation at the film/substrate interface; the corresponding design parameters include the thickness of a "compliant" substrate that can relax parallel to the interface and the compositional grading of the epitaxial film. The upper right insert of Figure 2 highlights a transferable, serial multiscale modeling strategy that links atomistic simulations of structural and compositional relaxation with continuum elasticity and dislocation theory for the study of interfacial stability, deformation behavior, film surface morphology, and strain relaxation kinetics (Zepeda-Ruiz et al., 1999). Continuum theory provides a parameterization scheme for atomistic simulation results. The resulting quantitative continuum description can be used very efficiently to carry out accurate parametric studies of strain relaxation and defect-free interface stability toward optimizing substrate thickness and epitaxial film composition. A representative experimental study of InAs epitaxy on GaAs(111)A, guided by the above modeling strategy, agreed excellently with the theoretical predictions (Nosho et al., 1999); InAs/GaAs is characterized by a high compressive lattice-mismatch strain of about 7% in the InAs epitaxial film, and it was chosen as an excellent prototypical system for this study. This modeling strategy is applicable to a wide class of heteroepitaxial systems.

The competitive advantage for chemical engineers

Multiscale materials modeling provides a powerful tool for fundamental understanding and quantitative prediction of complex materials behavior and has tremendous potential for technological impact in the microelectronics and optoelectronics industries. This belief is shared by colleagues in academia and in industry; the ever-increasing capabilities of high-performance computing strengthen this belief and fuel a growing modeling interest in both settings. Chemical engineers are uniquely positioned among other scientists and engineers to make significant contributions to the field of multiscale computational materials science. This is due to the *breadth* of our discipline that spans the spectrum from fundamental chemistry to chemical process modeling and process system engineering. Integration over widely different scales is an important part of our professional identity and culture: this is our competitive advantage. This alone, however, is not enough: *depth* of analysis at each scale is a requirement of primary importance. Additional elements of applied and numerical mathematics, statistical mechanics, and solid-state physics superposed on our traditional background will guarantee our competitiveness and ultimate success in this field. In turn, our attitude toward incorporating these extra elements will determine if computational materials science will emerge as a major new thrust within chemical engineering.

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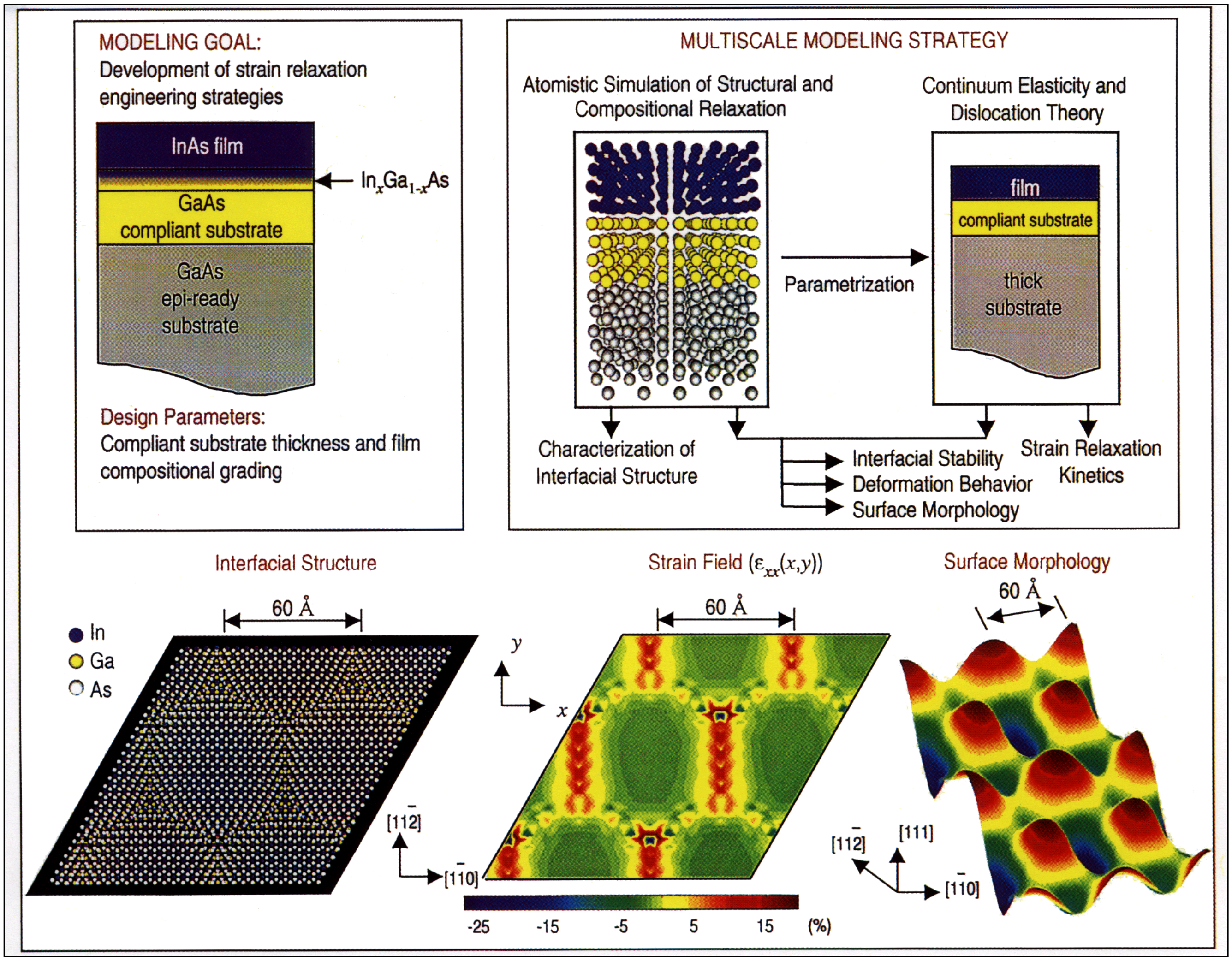

Figure 2. Multiscale modeling scheme for prediction and optimization of the strain relaxation behavior of an InAs/GaAs heteroepitaxial film/substrate system and the resulting structural quality of the epitaxial film. Representative computational results are shown for a semicoherent interface with a network of interfacial defects and the associated strain field and film surface morphology.

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