Electrochemical Engineering in an Age of Discovery and Innovation

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Introduction

Electrochemical phenomena play a central role in the fabrication as well as the functional capabilities of great many materials, processes, and devices . . .. from biological ion channels, to on-chip interconnections between transistors, and the spontaneous behavior of millions of corrosion sites on a metal as they interact to result in a catastrophic failure. The common feature of these example systems, along with a great many others, is that their behavior is largely determined as a result of concerted interactions based primarily on electrochemical phenomena that extend over many length scales.

Electrochemical phenomena control the existence and movement of charged species in the bulk, as well as across interfaces between, ionic, electronic, semiconductor, photonic, and dielectric materials. The existing technology base of the electrochemical field is massive and long-standing (Srinivasan and Lipp, 2003; National Materials Advisory Board, 1986). The pervasive occurrence of these phenomena in technological devices and processes, as well as in natural systems, is illustrated by several examples:

- *Materials* include metals, alloys, ceramics, ionic solids, semiconductors, membranes, coatings, colloids, conducting polymers, and biological materials including proteins and enzymes.
- *Phenomena* that arise include conduction, potential field effects, electron or ion disorder, electroluminescence, ion exchange, passivity, membrane transport, double layers at boundaries between phases involving free charges, osmotic flow, and electrokinetic phenomena.
- *Processes* that depend critically on these phenomena include energy storage and conversion, corrosion, membrane separations, electrodeposition, etching, desalination, electrosynthesis of chemicals, refining of metals, and many others.
- *Products* that result include microelectronic devices, sensors, batteries, fuel cells, coatings, films, metals, gases, chemicals, and ceramics.

During the past two decades, the field has evolved rapidly based primarily on a suite of remarkable new tools that provide the ability to create precisely characterized systems for fundamental study; to monitor behavior at unprecedented levels of sensitivity, atomic resolution, and chemical specificity; and to predict behavior with new theories and improved computational abilities. These capabilities have revolutionized fundamental understanding, as well as contributed to this rapid pace of discovery of novel materials and devices where product quality is determined at the molecular scale.

While new technological advances are today routinely envisioned, based on research in the bio-nano-micro and other fields, the manufacturability of such devices requires precise, quantitative understanding at a magnitude, sophistication, and completeness that is extraordinarily difficult to assemble today. These trends point the way toward future opportunities for ***molecular engineering*** which, as Carl Wagner observed 40 years ago (Wagner, 1962), "***may be important in the future development of industrial electrochemical processes***."

Discovery and Innovation: the Science Base

A renaissance is taking place in the field of electrochemistry. This science base is dynamic with many new ideas and discoveries based primarily on experimental work:

- Molecular electronic devices, launched 30 years ago by a proposal for unimolecular rectifiers (Aviram and Ratner, 1974), have seen significant recent progress (Reed and Lee, 2003) that includes the creation of additional components, such as wires, resistors, capacitors, amplifiers, etc., at the 1–2 nm scale.
- Molecular electronic junctions, in which electron transfer occurs from a conductor through a molecular layer to a redox component tethered to the electrode, have recently been demonstrated with carbon nanotubes (Avouris, 2002). The elucidation of charge-transfer processes was recognized by the 1992 Nobel Prize in Chemistry to Rudolph Marcus.
- Ion channels are proteins that serve as regulated nanoscale

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pathways for electrical current flow across membranes, with the additional ability to select among different ions as charge carriers (Hille, 2001). The Brownian dynamics of ion fluxes through channels have been simulated (Cooper et al., 1985) along with multiscale simulations that couple Brownian dynamics calculations for channel flux with electrostatics of ion-protein interactions for a single-occupancy channel (Jakobsson and Chiu, 1987).

- Organic light-emitting devices based on electroluminescence have advanced at a remarkable pace over the past decade, driven by their potential for significant impact on the information display market (Forrest, 2000; Friend et al., 1999).
- Anodized porous silicon exhibits significant carrier-confinement effects (Koshida and Matsumoto, 2003) that lead to remarkable properties including photoluminescence, electroluminescence, negative-resistance, nonvolatile memory, cold electron emission, thermally induced ultrasonic emission, and biodegradability related to enhanced surface activity.
- Thin film magnets have been formed from electrochromic materials, based on high Tc Prussian blue analogs electrochemically deposited on tin-doped indium oxide and glassy carbon electrodes (Sato et al., 1996).
- Charge transport and insulator-to-semiconductor transitions in double-stranded DNA were elucidated from electrochemical rate measurements for the electroreduction of H_2O_2 at soybean peroxidase-modified electrodes (Hartwich et al., 1999).
- The electrical potential has been shown to trigger specific switchable conformational transitions in single-molecular surface layers that alter important macroscopic properties, such as wetting, adhesion, friction, and biocompatibility among others (Lahann et al., 2003).
- A single-electron transistor operating at room temperature was recently fabricated by an electrochemical method involving localized anodic oxidation in a humid environment of smooth ultrathin Nb films on insulating SiO_2/Si substrates with use of a biased atomic force microscope tip to define source, drain, and gate (Shirakashi et al., 1998).
- Many novel nanostructures have been fabricated by electrodeposition (Hansen et al., 2002; Kolb, 2002; Lorenz and Plieth, 1998), including nanoclusters containing a few dozen atoms in precise locations and arrays (Engelmann et al., 1998; Kolb et al., 1999; Poetzschke et al., 1999; Ullmann et al., 1993; Ziegler et al., 1999), insertion of specific ions into specific molecular sites (Claye et al., 2000), atomic layer epitaxy (Stickney, 2002), as well as electrochemical fabrication of nanowires (Fasol, 1998; Fasol and Runge, 1997), nanocubes (Liu et al., 2003), superlattices (Switzer, 2001), and atomically layered nanostructures (Kothari et al., 2002) and materials having unique optical (Ali and Foss, 1999; Dang et al., 2000), magnetic (Kelly et al., 2000), and catalytic (Cheng and Dong, 2000) properties.
- The formation of abalone shells involves a hierarchical assembly of calcium carbonate that grows epitaxially in a layered structure that is mediated by the action of several proteins acting simultaneously over very wide length scales (Belcher et al., 1996). Attempts to replicate naturally occurring structures with synthetic systems are leading to ion-peptide systems that are remarkably similar to electrodeposition additives.

Electrochemical phenomena are at the center of these discoveries in high impact research fields. These discoveries will form the seedbed for new and innovative technological devices and processes that will represent the evolution of electrochemical engineering in the future.

Chemically reactive surfaces play a central role in determining the behavior, as well as the operating characteristics of an enormous variety of electrochemical systems. Precise control is invariably required of surface processes in order to form, manipulate, and stabilize the assembly of such systems—from new materials to medical implants and microelectronic devices—including many that are envisioned for nanotechnology applications (Drexler, 1992; Hoummady and Fujita, 1999; Lee et al., 2003; Prokop, 2001; Tsukagoshi et al., 2002). Nanotechnology will be increasingly used to assemble novel materials including functional materials (membranes and separators), hard materials (catalysts), and soft materials (additives and chemically modified surface films). By assembling nanostructured composites (involving semiconductors, conducting polymers, redox mediators, etc.), we will learn to manipulate pores with significant double-layer regions in order to achieve unique properties. Engineering methods for exploiting double-layer properties should grow in response to applications that use control at small scales, such as in electrophoretic and osmotic flows, microfluidics in MEMS, and colloidal and interfacial phenomena.

Biomedical and health care applications are deeply coupled to electrochemical phenomena, as are the very processes of life itself — action potentials, membrane and neurological phenomena, cell fusion, sensory and energy transduction, motility, and reproduction. These phenomena are based on interactions between ions, polyelectrolytes (e.g., proteins), or charged membranes containing enzymes and ion-selective channels. Technological applications will grow as engineers merge qualitative biological insights with quantitative engineering methods of analysis, many of which have been developed in electrochemical applications during the past 50 years.

Many additional growth areas could be mentioned as well, from energy storage and conversion with batteries and fuel cells, to environmental monitoring and waste treatment. Because the role of the electrical potential is ubiquitous at the small scale, where a great deal of scientific discovery and innovation is taking place, the electrochemical engineering community has a natural position of advantage for steering technology developments in the future.

Technology and the Engineering Base

The electrochemical technology base represents a major market force today with impact in three general areas: (a) as a major industry for materials and chemicals production; (b) as an enabling technology for other industries (such as batteries, and corrosion control); and (c) as a means of promoting well-being (such as health care and environmental fields). Many of the large-scale electrolytic technologies have been practiced for over a century. In some cases, electrochemical processes provide the only commercially viable means for production (as in aluminum, fluorine, chlorine, sodium hydroxide, copper, etc.).

While each electrochemical technology was tuned to the economic and technical realities at hand, similarities among many different processes may be recognized, the most significant being that, for economic reasons, ***large-scale electrolytic processes are invariably driven to a transport-limited rate***. Therefore, the electrochemical engineering research literature of the past 50 years focused strongly on understanding how ohmic and mass transport processes, including the effect of hydrodynamic flow, influence the potential field between electrodes as well as the current distribution, or rate of electrochemical reaction along a surface.

Current- and potential-distribution principles also were applied to electrochemical cells where corrosion occurs spontaneously by virtue of local anodic and cathodic regions that are driven by the energy contained in their local environment (Alkire and Verhoff, 1994). All structural metals are thermodynamically unstable and corrode. The annual cost of corrosion in the U.S. has been recently estimated to be \$276B, or 3.1% of the U.S. Gross Domestic Product (Federal Highway Administration, 2001). The principal applications involve paints, coatings and linings, plating and surface finishing, powder coatings, plastics, composites, flow control, water conditioning, water distribution, heating, fabrication, machinery, product finishing, pipeline, chemical processing, paper, aviation, automotive, nuclear and fossil fuel power, oil and gas, concrete, roads and bridges, ports, and public works. ***The design principles for corrosion are very different from those used in materials processing since, when you succeed in corrosion, nothing happens.*** The key requirement is to understand how failure occurs, and then to design so as to intervene.

Mathematical modeling of the current and potential distribution in electrochemical systems including corrosion has advanced steadily at the continuum level where sophisticated simulations are widely used to predict behavior and provide a rational basis for engineering design, scale-up, optimization, and process control (Newman, 1991). Continuum codes dominate the extensive modeling literature in electrochemical systems (Alkire and Chapman, 2003). A wide variety of phenomena can be included with the result that models are widely used for sorting out competing effects, resolving experimental data, articulating scientific hypotheses of mechanism, measuring system parameters, and predicting behavior. Such models provide a rational basis for engineering design, optimization, and control. Generally, however, they have been based on empirical characterization of the interfacial processes that appear as boundary conditions in the transport analyses.

The electrochemical field begins the century with an enviable record of accomplishments, many of which were carried out when the need was exceptional and the target was clear. Examples include:

- Electrochemical processes consume ~4% of the electricity generated in the U.S. The rapid escalation of energy costs during the 1970s motivated the introduction of new materials and cell designs, such as dimensionally stable anodes and membrane cells in the chlor-alkali industry. The impact of increased energy costs continues to be an important issue today.
- New membrane materials were developed for separation processes, artificial kidney dialysis, fuel cells, and water purification.
- The space program, as well as modern warfare and portable electronic devices, would be impossible without batteries. The early advances were followed by spectacular growth in sensors, more advanced batteries, and fuel cells.
- The accidental discovery of polyacetylene, along with subsequent research on doping it to achieve conducting properties ranging from an insulator to a semiconductor to a metallic conductor (Nigrey et al., 1981), led to the invention of "polymer batteries" based on polyaniline, as well as the awarding of the 2000 Nobel Prize in Chemistry to A. MacDiarmid, A. J. Heeger, and H. Shirakawa.
- Rechargeable lithium batteries are based on the ability of carbon to intercalate large quantities of lithium to form Li_xC_6 ($0<x<1$). The reaction of Li_xC_6 with nonaqueous solvents, to form a solid electrolyte interphase at the surface, plays an essential role in ensuring the stability and cyclability of such electrodes (Fong et al., 1990), which led to their subsequent widespread use in portable electronic devices.
- Cardiac pacemakers are powered by lithium/iodine-polyvinylpyridine batteries (Holmes et al., 1999), over five million of which has been implanted since 1972. Sensors based on electrochemical techniques are used for a very wide range of *in vivo* measurements including glucose, specific ions, and biologically significant materials.
- Microelectronic applications are intimately related to electrochemical fabrication operations in on-chip metallization, flat panel displays, and packaging. The shift from Al to electrodeposited Cu films for on-chip interconnections (Edelstein et al., 1997; Gwennap, 1997) represented one of the most important changes in materials that the semiconductor industry experienced since its creation (Andricacos, 1999). Figure 1 illustrates multiple layers of electrodeposited copper wires (the noncopper materials have been etched away) that provide the on-chip 3-D network for interconnecting the transistors.
- Magnetic data storage is a \$600B industry, based on the use of thin film heads fabricated by electrochemical methods since 1979, has seen steady reduction in cost by a factor of 10^7 to about \$0.001/Mbyte today.
- Analysis of well-characterized electrochemical systems, particularly microelectrodes and the rotating disk systems, were critically important to the development of quantitative

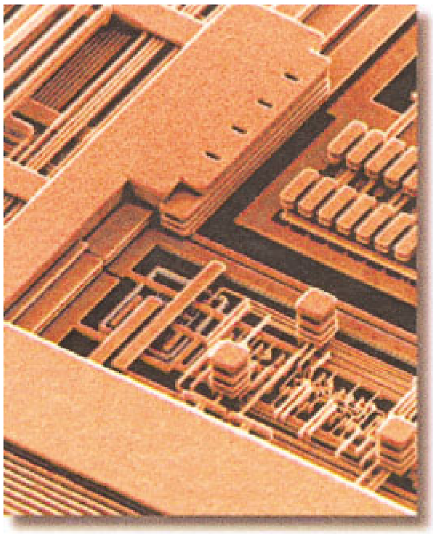

Figure 1. Multiple layers of electrodeposited copper wires (the non-copper materials have been etched away) that provide the on-chip 3-D network for interconnecting the transistors.

Copper interconnect technology was introduced by IBM in 1998, and is now widely used throughout the industry. Photo Tom Way and Ginger Conly. Courtesy of International Business Machines Corporation. Unauthorized use not permitted.

methods for the fundamental study of electrochemical reactions.

The most difficult physical situations encountered by continuum methods arise when there are coupled phenomena, where many length and timescales are important simultaneously, when events throughout the volume are important simultaneously with events at the surface, when the chemistry is complex and involves many species and many reactions, and when the surface is covered with a film. These aspects, which have been intractable to date, are yielding steadily to increased computing power and improved algorithms and software.

Modern Electrochemical Engineering: The Bridge from Molecular Phenomena to Macroscopic Processes

New applications in materials, medicine, and computers are being discovered where the control of events at both molecular and macroscopic length scales is critical to product quality. In addition, improvements in many economically significant electrochemical systems are today based on understanding how to control events occurring at near-molecular length scales. ***To drive the new electrochemical discoveries toward technology innovation, new science and engineering tools are needed in order to ensure product quality at the molecular scale***. Recent advances in computer speed and memory, numerical algorithms, and sensor technologies suggest that a systematic approach is possible that integrates scientific knowledge, intuition, experimental data, and simulations. However, engineering design tools based on continuum phenomena have a blind spot at the molecular scale (Alkire and Verhoff, 1994, 1998). Moreover, the primary manipulation during manufacturing today occurs at macroscopic length scales, for example, by controlling the electrolyte composition, temperature, fluid flow, mass transport, or potential field between electrodes. A new generation of science and engineering design methods must emerge to integrate discoveries, concepts, theory, and experimental data with process engineering in order to design and control future multiscale electrochemical systems (Alkire, 2003; Alkire and Ratner, 2003).

The challenges to building such tools include uncertainties in the physicochemical mechanisms, as well as the values of thermodynamic and kinetic parameters, complexities 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 tools to address systems described by noncontinuum and dynamically coupled continuum-noncontinuum models. These challenges specify the requirements for next-generation tools needed for a systematic approach to the design and control of electrochemical systems from molecules to devices.

To make the description of the challenges as concrete as possible, illustrative examples from the areas of electrodeposition and corrosion will be discussed. These applications share several common features with a wide range of engineering applications so that they represent good candidates for the development of improved engineering procedures: (a) mechanistic information is uncertain although multiple reasonable hypotheses of behavior are available in the literature; (b) critical events are difficult to observe directly by experiment, with the consequence that indirect measurements (largely carried out at several different scales) are used; and (c) the problems are multiscale and multiphenomena in nature and span from molecular details of surface chemistry and structure formation, to macroscopic aspects of transport processes and reactor/field conditions.

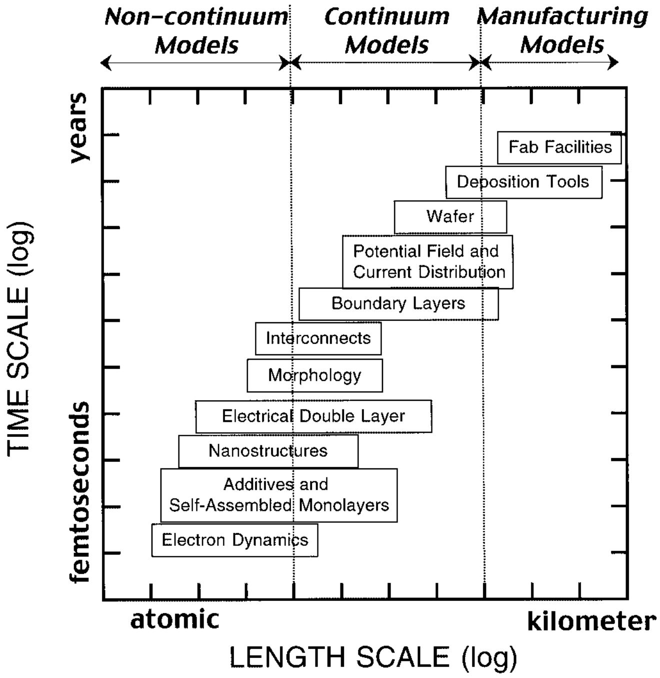

Figure 2. Range of time and length scales for electrochemical processing for chip manufacture (Alkire and Verhoff, 1998).

Numerical simulation methods are listed at the top.

Figure 2 shows the broad range of time and length scales—over 15 orders of magnitude—that are encountered for one particular field of application involving electrochemical processing for chip manufacture. Multiscale simulation links these time and length scales to understand interactions within an entire system (Maroudas, 2000). The sustained increase in both computing power and algorithm development is opening up revolutionary new computational-based approaches for research and technology development. ***To keep pace, simulation algorithms and systems tools need to evolve to allow for the deep integration of computational methods with the advancement of physical knowledge and its rapid transfer into innovative technological applications***. The challenges posed by multiscale systems specify the requirements for these tools.

Consider the effect of chemical additives on the evolution of the morphology of a copper surface during electrodeposition, particularly, how they may be "tuned" to achieve desired patterns during early stages of nucleation and initial growth. Such events are of central importance to the introduction of Cu for on-chip interconnections (Andricacos, 1999; Edelstein et al., 1997; Gwennap, 1997), shown previously in Figure 1, for which electrodeposition events at the nanoscale determine product quality, reliability, clock speed, and cost (Andricacos et al., 1998). In this process, an applied potential is used to electrodeposit copper on surfaces, and in trenches and vias. The

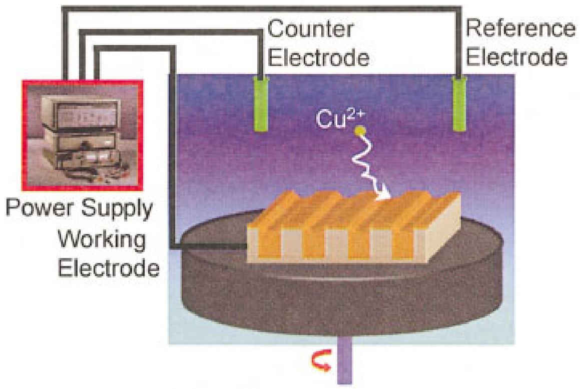

Figure 3. Electrochemical process for manufacturing on-chip interconnects, in which a rotating disk creates a boundary layer above the wafer surface (not drawn to scale).

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.

Figure 3 shows 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 (Andricacos, 1999; Andricacos et al., 1998), the precise physicochemical mechanisms of the interactions of these additives with the copper surface are not well understood (Datta and Landolt, 2000; Kondo et al., 2004; Moffat et al., 2000, 2001, 2004; Tan and Harb, 2003; West, 2000), 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. ***Tools for constructing models for these systems must be able to address uncertainty in physicochemical mechanisms, as well as uncertainty in parameters***. This motivates the quantification of uncertainties in the models for these processes, and the linking of experimental data with sensitivity analysis, parameter estimation, and model selection tools to select among competing hypothesized mechanisms.

Another challenge of these systems is that the codes used to simulate these systems are computationally expensive. Advanced numerical models for corrosion processes include consideration of chemical species that interact through participation in reactions at the surface, as well as in the volume, along with transport by diffusion, migration, and convection. The models typically consist of a set of coupled nonlinear partial differential-algebraic equations (PDAE) that can be extremely stiff. ***The trend toward increasingly sophisticated models that integrate diverse phenomena, which span multiple scales for simulating entire realistic systems, creates significant demand for new simulation algorithms with improved computational efficiency, and with realistic quantification of uncertainty.*** These requirements include algorithms and software for the efficient solution of extremely stiff and large-scale PDAE systems for simulating bulk phases, as well as for extracting information from large-scale simulations, and making use of it for assessing proposed mechanisms.

The algorithmic needs become even greater when noncontinuum models are involved. For example, consider Figure 4, which shows a multiscale simulation model for the electrodeposition of copper into trenches. While the chemical reactions and the diffusion and migration of species in the solution boundary layer are described by a PDAE system, the nucleation, surface chemistry, and roughness evolution of the trench surface are most accurately simulated using noncontinuum methods, such as kinetic Monte Carlo (KMC) simulation (Battaile et al., 1997; Drews et al., 2004a; Henkelman and Jónsson, 2001; Levi and Kotrla, 1994; Yang et al., 2002). Figure 4 shows the infill of several trenches simulated using a 3-D KMC code, that tracks adsorption, desorption, bulk and surface diffusion, and chemical reactions (Drews et al., 2004bc). To reduce the computational load, the 3-D KMC code was coarse-grained (Gear et al., 2003; Ismail et al., 2003a,b; Jönsson et al., 2003; Lopez et al., 2002; Shelley and Shelley, 2000), such that clusters of molecules were tracked instead of individual molecules (Drews et al., 2003b; Katsoulakis et al., 2003; Katsoulakis and Vlachos, 2003; Pricer et al., 2002ab). Even with these simplifications, it takes ~1 day to perform one simulation run. This greatly limits the number of simulation runs that can be made during iterative calculations for estimated parameters from experimental data or using the model in optimization algorithms for design or control. ***Tools for analyzing and optimizing multiscale systems must be more computationally efficient than most existing systems tools.*** As a further complication, the codes in Figure 4 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 simulation and systems tools must be able to handle models described by dynamically coupled continuum and noncontinuum codes.***

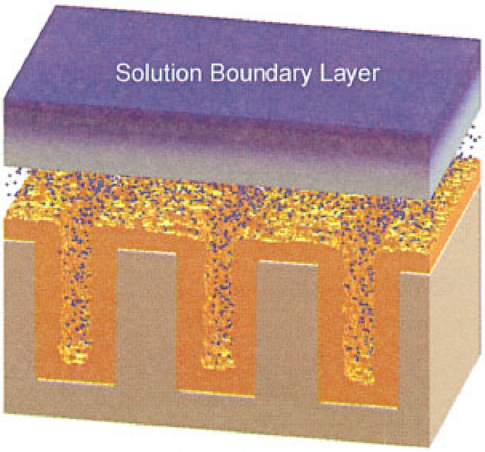

Figure 4. Mulitscale simulation of the electrochemical process for manufacturing on-chip copper interconnects (not drawn to scale).

The dots represent Cu^{2+}ions in solution, with the film on the surface being metallic copper.

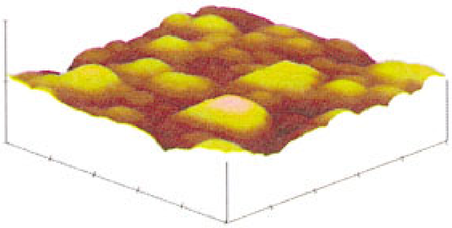

Figure 5. Atomic force microscopy image of an electrodeposited copper surface.

Another challenge in electrochemical 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 occur with many uncertain parameters. The key measurement data, which are atomic force microscopy images, are only available at the end of the process (see Figure 5). This motivates the design of high-throughput experimental techniques to maximize the range of operating conditions, and the quantity of experimental data, and experimental design methods that maximize the information from sensors, to create models that are predictive. This also motivates the creation of large data libraries to be mined to develop and refine hypotheses of mechanisms.

Another challenge 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 Figure 3 is the applied potential, which does not provide enough degrees of freedom to produce void-free copper in the 0.13 mm trenches used in modern microelectronic devices. This is why 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 modern electrochemical systems require that molecular and nanoscale manipulation be treated as a design focus, to exploit self-assembly during processing.***

The above challenges indicate that multiple hypothesized mechanisms and operating conditions need to be explored to develop a predictive model. This motivates the use of software implementations for the simulation codes that make it easier to change hypothesized mechanisms, model assumptions, chemical specifications, operating conditions, and system geometry without rewriting or recompiling the codes.

Concluding Remarks

The field of electrochemical science and engineering is undergoing a renaissance, owing to discoveries and innovations in a wide variety of fields that involve the existence and movement of charged species in bulk phases, as well as across interfaces between phases. The existing technology base of electrochemical application is enormous. The combination of new practical applications along with improvements in the traditional industrial base provides a rich set of engineering challenges.

Such activities will require the linking of traditional engineering tools with the noncontinuum scale, particularly where product quality is determined at the molecular scale. It is especially important to encode advances in physical understanding of molecular phenomena into numerical simulations of the entire system, not just the components, in order to design and control technological systems.

The ability to use multiscale, multiphenomena numerical simulations to achieve precise, quantitative understanding at new levels of magnitude, sophistication, and completeness offers a challenge for electrochemical engineering which, when met, will bring enormous benefits through rapid innovation, as well as improvements in existing technological applications.

While many research groups have started to address these challenges posed by modern electrochemical systems, the opportunities for impact are far greater than the current researchers can accomplish. This article hopes to inspire more individuals to move into this intellectually challenging and economically significant field.

Acknowledgments

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