Biomolecular Self-Assembling Materials

by Philip Pincus, Chair, Panel on Biomolecular Materials

The Panel on Biomolecular Materials recently completed a report on this dynamic new area at the interface between physics and biology. This article summarizes the report. The full report is available with color illustrations at the BPA’s website (www.nas.edu/bpa) and in printed form from the BPA office.

Research on self-assembling biomolecular materials is an exciting new discipline lying at the intersection of molecular biology, the physical sciences, and materials engineering. Biomolecular materials are those whose molecular-level properties are abstracted from biology. They are structured or processed in a way that is characteristic of biological materials, but they are not necessarily of biological origin. For example, the structure of a man-made ceramic material may be based on that of a clam shell, or a synthetic polymer may be produced using techniques from molecular biology that were originally developed for working with proteins.

A key feature of biomolecular materials is their ability to undergo self-assembly, a process in which a complex hierarchical structure is established without external intervention. Self-assembly is common in biological materials. For example, long protein molecules fold themselves into complicated three-dimensional structures, and certain lipid molecules align themselves with each other to form membranes.

The focus of this report is the study and generalization of biomolecular self-assembly, with the ultimate goal being the development of new materials of technical importance. The underlying theme is the belief that there are important lessons to be learned from understanding, and perhaps mimicking, biological materials found in nature and the ways in which they self-assemble. In nature, experiments on biological materials have been going on for millions or even billions of years, and it is up to us to understand them better and learn how to profit from them.

If the principles of biomolecular self-assembly can be extended to the control of modern materials synthesis, they will lead to a broad range of new materials and processes with significant technological impact. The approaches used can be expected to fall into two general categories. The first involves directly mimicking biological systems or processes to produce materials with enhanced properties. An example of this approach is the use of molecular genetic techniques to produce polymers with unprecedentedly uniform molecular length. The second category involves studying how nature accomplishes a task, or how it creates a structure with unusual properties, and then applying similar techniques in a completely different context or using completely different materials. An example of this approach is the study of the laminated structure of clam shells, See “Biomolecular Materials” on Page 2

Database Needs for Modeling and Simulation of Plasma Processing

by David B. Graves and Mark J. Kushner, Cochairs, Panel on Database Needs in Plasma Processing

We chaired a panel that recently completed a report on database needs for modeling and simulation of plasma processing. The main purpose of this report is to highlight the opportunities for more rapid and effective development of plasma process modeling and simulation as an engineering tool in the semiconductor manufacturing and plasma equipment supplier industries. It is intended for a variety of audiences: academic and government laboratory researchers, industrial engineers and scientists, and program managers at federal funding agencies.

The scope of the report is substantial, covering the industrial needs for better plasma process engineering, the current state of the art in plasma modeling, and the various supporting databases and diagnostic techniques that underlie and complement modeling and simulation. The report begins with a chapter on industrial perspectives to emphasize the primary purpose of this study: to serve the needs of industrial suppliers and users of plasma process equipment. The need to maintain this industrial perspective is a recurring theme of this report.

The potential for using modeling and simulation to benefit industrial users of plasma processes and equipment has never been greater. Computational costs continue to decrease steadily, and in the last several years, considerable progress has been achieved in establishing the major modeling strategies that are necessary to achieve practical industrial objectives. Nevertheless, low-temperature plasma See “Plasma Processing” on Page 4
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which has been reverse-engineered to design a metal-ceramic composite twice as strong as other composites and an order of magnitude tougher, and constructed of more robust materials than its natural analogue. An important finding of this report is that successful application of biomolecular techniques could have a significant impact on materials and processes.

The Panel on Biomolecular Materials has identified a number of long-term scientific and technological opportunities in the field. Molecules that form liquid crystals can be incorporated into polymers to produce materials that have useful optical properties, are easily processed, and have good mechanical properties. Membrane-based structures can be used in applications ranging from controlled release of drugs to ultrafiltration to biosensors. It may be possible to design self-assembling electronic devices. New synthetic polymers and new polymer synthesis techniques are possible, including the production of protein- and polyester-based polymers from biomass. Biomolecular sensors may find applications in health care, agriculture, ensuring food quality and safety, and the detection of biological warfare agents. Biomotors may be developed that can construct biomolecular structures on a unit-by-unit basis.

The panel has concluded, however, that the existing infrastructure for research on biomolecular materials is not keeping pace with the development of these opportunities. As time passes, and as the record of significant results grows and the potential economic impact becomes more apparent, the need for new infrastructure only becomes more acute. The panel has therefore concluded that the existing system of disciplinary, individual-investigator-based excellence in research and education should be augmented.

Specifically, the panel has identified the following four options that could help to stimulate progress in the field:

1. Interdisciplinary collaborations could be encouraged by a new mode of research through which small numbers of scientists would come together to work on a specific problem, such as the ones identified in this report. This mechanism would encourage new collaborations while keeping their size small to help ensure accountability.

2. Consortia in biomolecular materials could be developed, i.e., groups of investigators that are focused on a specific theme or a specific instrumental capability. Such groups could involve scientists at a particular site such as a university campus or a government laboratory, or they could be consortia involving several sites. They would vary in size but would each have a well-defined focus: specific instruments, particular scientific problems, or a defined technological goal. Pre-existing collaborations with established track records of interdisciplinary activity should be favored in establishing these groups. Some of the groups could be built into existing structures such as the Materials Research Laboratories (MRLs), Science and Technology Centers (STCs), and government laboratories. Groups that have special facilities should be open to external scientists. Geographical dispersion could be a component in the selection criteria. Incorporation of the government laboratories into the groups should be strongly encouraged since the government laboratories house a broad spectrum of instruments, experience in instrument development, and relevant expertise in such areas as synchrotron radiation, neutrons, imaging (electron microscopy, scanning tunneling microscopy, atomic-field microscopy, and x-ray microscopy), and chemical and biological synthesis and characterization.

3. Academic programs could be established at universities to encourage curriculum development and training in biomolecular materials. These programs would bridge biology, materials science, and the physical sciences. The multidisciplinary character of
biomolecular materials research, though in many ways a great strength, can be a barrier for students pursuing an education in the field. New academic programs and curriculum development could help to overcome this problem. It is important that students be trained in one of the disciplines in depth, however, obtaining interdisciplinary breadth during the research phase of their graduate careers.

One way to support such training could be the provision of special training grants like those that NIH has recently provided in areas related to biomaterials. Any such grants should include requirements for additional courses as well as for a program of research. The panel believes that the effectiveness of such a grant program would be enhanced if institutions receiving grants were encouraged to strengthen their ties with government and industrial laboratories. For example, they could make arrangements for outside laboratories to provide summer jobs for their graduate students, and the participating government and industrial researchers could host visitor programs and serve as guest lecturers at the universities receiving the grants.

4. A national Biomolecular Materials Institute (BMI) could be established, located at a university or a government laboratory or another site with an appropriate intellectual environment. Like options 1 and 2 above, this option is motivated by the panel’s consensus that interdisciplinary collaboration requires special support and encouragement. For example, in the study of many aspects of biomolecular materials, such as those described above for molecular machines, close interaction between researchers is both difficult and very important. In addition, a national institute would broaden access to instruments and research facilities, facilitate contacts between the academic community and private industry, and enhance the visibility of the field in a way that would encourage the creation of university programs in biomolecular materials research and education.

A national BMI would act as an umbrella organization for the field. It would have four main tasks:

a. To examine research directions through workshops, meetings, and studies, giving particular attention to proposed novel initiatives;

b. To encourage interdisciplinary collaborations by bringing together scientists and engineers from different backgrounds, e.g., different disciplines or affiliations;

c. To provide instrumental facilities that would encourage interactions between experimental groups; and

d. To provide industry with a single contact point for obtaining information about biomolecular research activities and for obtaining assistance in making connections with those activities.

Structurally, the BMI might resemble the NSF-sponsored Institute for Theoretical Physics in Santa Barbara. For example, it would have quasi-independent status and be overseen by a broad-based advisory board. It would consist of a small cadre of permanent scientists, plus staff commensurate with the above-listed tasks, such as experts to assist visiting scientists in using the instruments and laboratories. Funding should if possible be provided in at least five-year increments, either by a single agency or preferably by a consortium of agencies such as NSF, NIH, the Department of Energy, and the Department of Defense. Funding should also include substantial industrial support if at all possible, probably at about the 25% level.

Although this option may be difficult to achieve in the current funding environment, the panel believes it is an important goal for the future.
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processing science is a relatively young field, and it has not therefore received the in-depth, sustained attention that is required to have a significant, timely impact in industry.

This situation is perhaps most evident in the area of the database for physical and chemical processes in plasma materials processing. The data that are currently available are often scattered throughout the scientific literature, and assessments of their reliability are usually unavailable. The goals of this report include identifying strategies to add data to the existing database, to improve access to the database, and to assess the reliability of the available data. In addition to identifying the most important needs, this report assesses the experimental and theoretical/computational techniques that can be used, or must be developed, in order to begin to satisfy these needs.

A major complication in this process is the fact that industry uses a large variety of gases and materials in plasma processes and equipment. Since time and resources are always limited, one must make choices regarding which chemical systems to examine carefully. Experiments are expensive and time-consuming, and therefore it may be necessary to augment these measurements of fundamental data with theory. Computational techniques are useful, but may require careful testing since the methodologies are sometimes not fully mature. The panel has attempted to develop a compromise between the competing needs for breadth and depth in the database, recognizing that needs change as industry evolves. The recommendations presented here will therefore require updating, probably within 3 to 5 years of the publication of this report.

Executive Summary

The 1991 National Research Council (NRC) report Plasma Processing of Materials: Scientific Opportunities and Technological Challenges included a projection that worldwide semiconductor sales would double from $50 billion in 1990 to $100 billion in 1995. In fact, total sales worldwide for semiconductors passed $140 billion during 1995, nearly triple the 1990 level. Companies that supply plasma equipment to the semiconductor industry have experienced similar, if not greater, rates of growth. Plasmas in one form or other are used in about 30% of all semiconductor manufacturing processing steps, and about the same fraction of processing equipment is plasma-based in a typical microelectronics fabrication facility. An important trend accompanying this growth in the industry is the fact that the capital cost of constructing a new microelectronics fabrication facility is similarly escalating and is now on the order of $1 billion or more. Estimates are that over 60% of this capital cost is for processing equipment, including plasma equipment. Processing equipment design, optimization, and control therefore take on added importance, because equipment depreciation accounts for a significant part of the price of a chip.

In spite of its high cost and technical importance, plasma equipment is still largely designed empirically, with little help from computer simulation. Plasma process control is rudimentary. Optimization of plasma reactor operation, including adjustments to deal with increasingly stringent controls on plant emissions, is performed predominantly by trial and error. There is now a strong and growing economic incentive to improve on the traditional methods of plasma reactor and process design, optimization, and control. An obvious strategy for both chip manufacturers and plasma equipment suppliers is to employ large-scale modeling and simulation. The major roadblock to further development of this promising strategy is the lack of a database for the many physical and chemical processes that occur in the plasma and especially at surfaces. Although a complete set of data for all gas phase and surface processes for all species present in the plasma is not necessary for many applications, the current lack of detailed information concerning the vast majority of processes and species is the major factor limiting the effectiveness of models. Given the reality of inevitably limited resources, and the often considerable investments that must be made to measure or compute collision cross sections, reaction-rate coefficients for gas-phase reactions, and surface chemical rates at surfaces exposed to plasma, some priorities must be established. These priorities are discussed below, and the report’s recommendations on priorities constitute one of the main results of the study.

Findings

1. The integrated circuit (IC) manufacturing industry remains in its historical pattern of rapid technological change, and this pattern has begun to seriously challenge plasma equipment suppliers to continue the trend toward ever higher performance/cost ratios. Plasma processing tools are, in most cases, designed and optimized empirically. Real-time control of plasma processes has not been adopted by the industry. Further improvements in performance by means of empirical adjustments will soon reach a point of diminishing returns, if they have not already.

2. Control of processes in plasma reactors must occur on length scales that range from tens of angstroms to tens of centimeters and time scales that range from seconds to tens of hours. Loss of control at any point in this spectrum of length and time scales can result in reduced yields of components and therefore significant economic losses. For example, precise control of transistor gate and metal wiring levels across the entire chip is necessary to manufacture microprocessors at the highest speeds. Loss of this control over etching precision produces slower microprocessors and a loss of hundreds of dollars per chip.
Obviously, across-wafer control is equally important to maintain high yields and therefore high profitability.

3. Models of low-temperature, nonequilibrium plasmas, especially for the description of physical phenomena, have developed rapidly in the last 5 years. Computing power per unit cost continues to increase rapidly. However, few of the currently available plasma models can be easily used by process engineers. Although attempts have been made to model plasmas with realistic chemistries, the parameter space that can be addressed is limited. Only a handful of studies have been made that attempt to validate models of plasma processes with industrially relevant chemistries. Models that attempt to link the relevant length scales (from tool scale to feature scale to atomic scale) are just now emerging. Simulations can be no more accurate than the data and assumptions on which they are based. The lack of fundamental data for the most important chemical species is the single largest factor limiting the successful application of models to problems of industrial interest.

4. Heterogeneous (surface) processes are at the heart of plasma materials processing technology, but are in many cases much less well understood than are gas phase processes. Numerous etching and deposition profile evolution simulations are used in industry. These simulations generally use empirically derived rate coefficients that must be refitted to experimental data whenever conditions change. Experimental diagnostics and modeling of plasma-surface processes based on first principles are rudimentary and require much development. Surfaces exposed to plasmas are often strongly modified by intense ion, photon, and radical species bombardment. Therefore, not only are the chemical and physical processes themselves strongly perturbed by plasma exposure, but in addition, the surfaces upon which the processes take place are unconventional in their structure and composition.

5. Electron-collision cross-section data are second only to data on heterogeneous processes in their importance to plasma processing. These data are sketchy at best for most species of interest, although some key species, such as SiH₄ and CF₄, have received considerable attention. Little information is available for dissociation products or for species in excited states. Recent progress in computational methods based on quantum scattering offers the possibility that the costly and time-consuming experiments may be augmented or even replaced by large-scale computer calculations.

6. There now exists a wealth of chemical species in the plasma or on the surface. Spectroscopic measurements are usually the first step in measuring a rate coefficient or in testing a model prediction. The spectroscopic database therefore serves a dual role to provide both qualitative and quantitative information. Although the spectroscopic database is far from complete, especially for surface species, data are available in the literature that are relevant to plasma processing. However, these data are scattered throughout the technical and scientific literature, and in some cases their accuracy is in doubt. The ready availability and ease of spectroscopic database manipulation and storage will stimulate the development of new diagnostic techniques and the wider application of existing methods.

7. The database for ion-molecule and neutral-neutral chemistry varies considerably. For some species and reactions, the data are good. This is especially true for the cases in which there is overlap with processes occurring in the upper atmosphere or in some cases in chemical vapor deposition processes. In other cases, however, most notably for etching processes, there are few data available.

8. thermochemical data are sketchy for many species of interest in plasma processing. These data are important in helping to establish boundaries for reaction pathways and for estimating reaction rate coefficients. Techniques, both experimental and computational, are generally available to obtain these quantities, but few efforts are under way at present to meet these needs.

Conclusions

1. The major potential benefits of plasma modeling for chip manufacturers are better control over plasma processes, minimization of resources that would otherwise be devoted to optimizing plasma processes, and possibly minimization of problems associated with undesirable emissions such as greenhouse gases and ozone depleters.

2. The major potential benefits of plasma modeling to plasma equipment suppliers include more rapid and efficient development of new tools that meet increasingly stringent process requirements, optimization of designs before fabrication of prototype tools, and development of robust, real-time process control schemes for their tools.

3. The main roadblock to development of plasma models that will have these industrially important uses is the lack of fundamental data on collisional, reactive processes occurring in the plasma and on walls bounding the plasma. Among the most important missing data are the identities of key chemical species and the dominant kinetic pathways that determine the concentrations and reactivities of these key species, especially for the complex gas mixtures commonly used in industry.
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4. The lack of a central location to collect, analyze, and disseminate the data that are currently available, or that will be available in the future, is a serious problem.

5. Large numbers of materials and chemistries are used in plasma processes for integrated circuit manufacturing. Given the reality of inevitably limited resources, it is necessary to establish priorities that encourage development of relevant data for only a few of the most important chemistries, both currently and for the next 5 to 10 years.

**Recommendations**

1. Federal funding agencies should make greater and more systematic efforts to support development of an improved database for plasma modeling. In addition, given the direct benefits an improved database would provide for both semiconductor manufacturers and plasma equipment suppliers, organizations set up by industry to promote integrated circuit manufacturing and the semiconductor equipment industry should participate in supporting targeted database development. Greatest emphasis should be placed on surface processes because of their centrality in the technology and because this is the area in which in general the least is known. However, the other database needs outlined in the main text of this report—electron-collision processes, spectroscopic/radiative processes, ion-neutral and neutral-neutral chemistry, and thermochemistry—are also important and need considerable work if the models are to achieve their potential impact industrially. Computational approaches to providing database information, using *ab initio* electronic structure codes as well as semiempirical methods, should be encouraged.

2. A spectrum of plasma models should be developed, aimed at a variety of uses. One set of codes should be developed to provide a compact, relatively fast simulation that addresses plasma and surface kinetics and is useful for process engineers. Convenient user interfaces would be important for this set of codes. A second set of codes would include more sophisticated algorithms and higher dimensionality, and would be more useful for equipment design. Development and testing of models that meet these needs should be supported. Careful validation of the codes by systematic comparison to the results of experiments needs to be undertaken. As learning and resources allow, some development effort should focus on fully three-dimensional plasma, electromagnetic, and neutral transport codes. The degree of chemical complexity to be included will vary depending on the availability of data, the goals of the modeler, and the available computational resources.

3. The following chemistries and materials should have a high priority in database development. The panel chose these systems because the applications are currently important and are anticipated to continue to be important for at least the next 5 years and quite probably beyond that:

   a. Polycrystalline silicon etching in chlorine-containing gases and bromine-containing gases. This set (of materials and chemistries) is commonly used in the etching step to define the gate electrode in field effect transistors. Control of this step is crucial in maintaining optimum device performance, and since at endpoint this step involves exposure of the increasingly thin gate dielectric, concern about damage and reliability is considerable for this step.

   b. Silicon dioxide etching in fluorocarbon-containing gases mixed with gases such as O₂, H₂, CO, He, and Ar. In back-end-of-the-line (BEOL) processes, one is mainly concerned with making the metallic interconnects inside a silicon dioxide insulator. The number of interconnect levels is rising, and the number of steps that involve contact (to the active device regions) and vias (from one level of metalization to the next) will increase accordingly. Concern here is with anisotropy, selectivity, and uniformity, as well as with contamination. These gases are also used to clean chambers that have been coated with dielectric films (silicon dioxide and silicon nitride) from previous steps using chemical vapor deposition (CVD). In addition, since many of the gases that are used for dielectric etching are currently of environmental concern because they are greenhouse gases (e.g. C₂F₆), an opportunity exists to minimize their use, remediate them as effluents, or even to replace them outright, if effective models of dielectric etching can be developed.

   c. Silicon dioxide deposition through plasma-enhanced chemical vapor deposition (PECVD), using mixtures of SiH₄, N₂O, and O₂, or SiH₄, O₂, Ar, and TEOS (tetraethoxysilane). For the same reasons that oxide etching will continue to play an important role in BEOL processing as the number of interconnect levels increases, deposition of the intermetal dielectric will be a key process.

4. At least one data center should be established to archive, evaluate, and disseminate the existing and future database for models of plasma materials processing in integrated circuit manufacturing. The archived database should include kinetic pathways, mechanisms, and comparisons of models to the results of experiments. This structure would provide a framework for iterative improvement of the database. Full advantage should be taken of emerging electronic data acquisition technology exploiting rapid access through the Internet and the World Wide Web. Although individual companies will no doubt develop proprietary databases, the goal sought with the establishment of the data center is to serve the entire community interested in plasma modeling and diagnostics.

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The Editorial Page

The New Congress and Issues in Science and Engineering

by James Jensen

The election has brought on few major changes for science and engineering. There will be some subtle differences in the voting and behavior of each house of Congress, and there will be some new chairs of key committees, but there is nothing to compare with the seismic shift that occurred in 1994.

The House of Representatives

In 1994, the Republicans had a majority of 18 seats. That has been reduced to about 10 seats. The exact outcome depends on runoff elections in Texas and a number of close races that will have to be settled by recounts, the results of some of which were not available at press time. One of the close votes settled by recount concerned Congressman Brown’s (D-CA) seat. He was declared the winner with a final margin of victory of 865 votes.

Working control of the House will shift toward the center. With the slimmest majority of control in decades, Speaker Gingrich will have to satisfy moderate Republicans and conservative Democrats to pass any legislation. Indeed, the moderate Republicans held press conferences within hours of the closing of the polls to declare their intent to have greater inclusion in the early drafting and strategizing on legislation. It seems likely that the effect will be to moderate the process in the House generally, as the committee chairs will also have slim majorities, and thus greater cooperation will be necessary to pass bills.

The change in committee chairs of most interest to the S&T community is that Congressman James Sensenbrenner (R-WI) will replace Congressman Robert Walker as chair of the House Science Committee. Mr. Sensenbrenner has concentrated on space issues in the past, particularly the question of manned space flight and the dangers of foreign participation in the space station.

Major changes in the R&D budget are probably not in the cards. Mr. Walker will no longer serve on the Budget Committee, but the real decisions are made by the authorization and appropriations committees, where the cast of characters will not change significantly.

The major question concerning the R&D budget still concerns the problem of constraining entitlements. The Republican leadership clearly intends to wait for the President to make the first move on entitlement reform. R&D will probably get approximately the same budget treatment that it received last year. The longer-term outlook depends on the outcome of efforts to constrain entitlements.

The strong economy is alleviating the deficit problem, to the delight of politicians everywhere. The deficit estimate for FY 1996 dropped from $195 billion to $106 during the course of the year, so a number of Congressional leaders are without a doubt hoping the economy will continue to grow long enough to obviate some of the hardest choices.

The Senate

The Senate, like the House, did not experience any historic shifts. The Senate had 53 Republicans and 47 Democrats in the 104th Congress. In the 105th, it will have a 55 Republicans to 45 Democrats. A significant number of departing members were centrist Democrats and moderate Republicans, who have been replaced in the aggregate by a more conservative group. While the changes are small, they could tip the scales. Two major initiatives of the Republican leadership were thwarted in the last Congress by a single vote—the constitutional amendment for a balanced budget and regulatory reform. The majority to pass such legislation may now exist, and Senator Lott has already announced his intention to bring up the amendment. The small changes put the 60 votes necessary to cut off filibusters nearer to Senator Lott’s grasp.

There are some important changes in committee chair assignments. Mr. Hatfield (R-OR), who chaired the Appropriations Committee for many years has retired and has been replaced by Senator Stevens (R-AK). While he will not necessarily adopt Senator Hatfield’s strong support of the National Institutes of Health, Senator Stevens has a keen interest in science and technology. Hatfield’s retirement might catalyze a reshuffling of appropriation subcommittee chairs. The Energy and Water Subcommittee (which appropriates funds for the Department of Energy) will be chaired once again by Senator Domenici (R-NM).

The Senate authorizing committee for most civilian science and technology agencies is the Committee on Commerce, Science, and Transportation. It was chaired by Senator Pressler (R-SD), who was defeated in his bid for reelection. The new chair will be Senator John McCain (R-AZ). Mr. McCain has devoted himself almost exclusively to aviation issues while on the committee, and we will have to wait to see what his broader science and technology interests will be. A more important factor may be whether Senator Burns (R-MT) continues as chairman of the Subcommittee on Science, Technology and Space.

James Jensen directs the National Research Council’s Office of Congressional and Government Affairs.
Recently Completed BPA Studies:

- *Biomolecular and Self-Assembling Materials.* Available from the Board on Physics and Astronomy (202-334-3520) and on the BPA website.

- *Database Needs for Modeling and Simulation of Plasma Processing.* Available from the Board on Physics and Astronomy (202-334-3520) and on the BPA website.


For up-to-date information on BPA activities and publications — See our website at www.nas.edu/bpa