Computer Modeling of Deposition and Etching

by E. Hyman and S. Eidelman

In the aerospace, automotive, chemical, electronics, and tooling industries, many operations rely on two processes: *deposition*, precision coating of one material on another; and *etching*, controlled removal of a material from its substrate. These processes can be used to develop improved materials for consumer products and defense needs, if we can maintain precise manufacturing tolerances in uniformity, consistency, coating quality or etch feature, and efficiency.

Unfortunately, the fundamental understanding of the physics and chemistry of these processes has been incomplete, so engineers have counted on experience and intuition in designing new deposition or etching equipment for special applications. Therefore, adapting a process to new-product requirements always entails considerable financial risk.

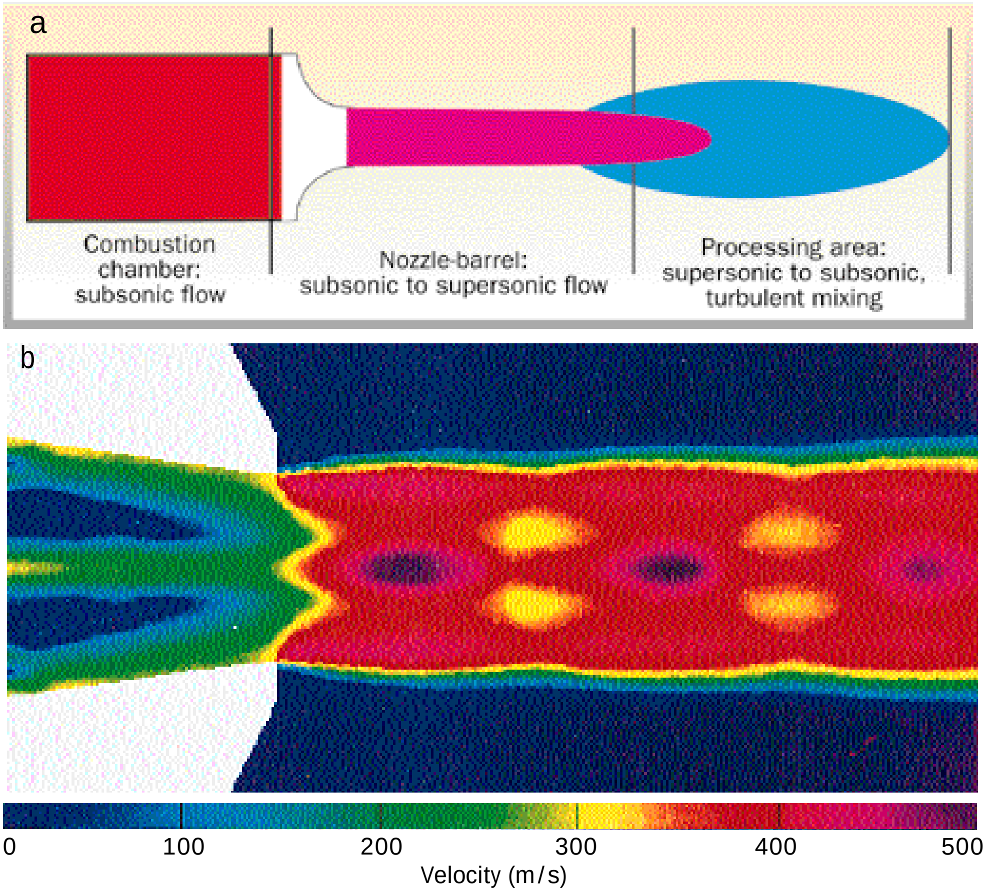

Figure 1. (a) Schematic diagram of a high-velocity oxygen-fuel thermal spray (HVOF TS) system. (b) Modeling results of HVOF TS system gas streams in cross section in the barrel and interacting to form the supersonic jet, which carries particles to the substrate. The color scale indicates velocity variations, from highest (magenta) to quiescent (black) flow.

That risk could be reduced by using computer modeling to examine alternative design concepts and to investigate different ranges for important parameters. Most computer models, however, have not captured enough of the complex physics and chemistry needed to make reliable predictions. Computer running time and memory requirements have forced modelers to treat limited aspects of a process or use idealized geometries, even though engineers know that a process may be extremely sensitive to such details.

In addition, some aspects of physics and chemistry have not been well enough understood to model reliably, although improved diagnostic capabilities show promise of providing needed information. As computer capabilities become greater and product requirements become increasingly stringent beyond the capability of intuition to guide process improvements, numerical models are likely to play a larger role in the future.

Industrial needs for reliability and for meeting product specifications require numerical-simulation tools that can be applied to a specific process. These tools must incorporate the real geometry of every design element that affects the process, and they must capture all the important physical and chemical processes. Inevitably, developing such tools is a large-scale, multiyear, multidisciplinary undertaking that must be accompanied by experimental studies, reactor diagnostics, and model validation. Such an undertaking surpasses the financial interest of individual industrial firms, even the largest ones, because the cost is too high relative to potential payback. On the other hand, developing such tools could provide immense benefits for industry collectively. Consequently, major government funding has supported such work.

The Department of Defense's Advanced Research Projects Agency (ARPA), for example, has supported modeling efforts here at Science Applications International Corporation (SAIC) and at Sematech, Inc., Austin, Texas. In addition, major computer codes developed at the Department of Energy's

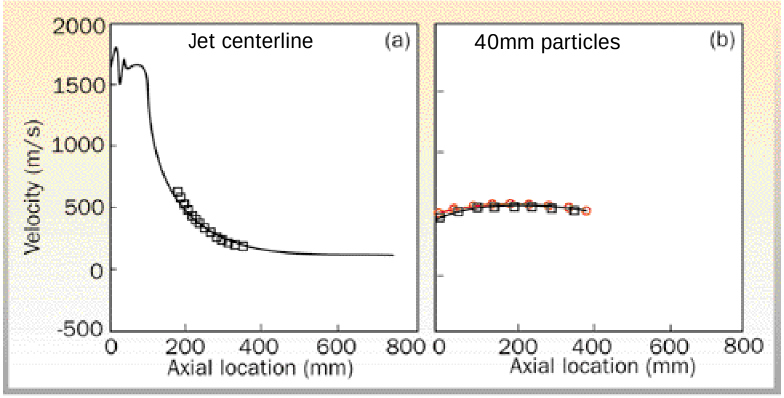

Figure 2. Comparison of experimental and simulated ○ gas-velocity distribution in an HVOF TS system.

Lawrence Livermore National Laboratory are being used to model etching reactors through cooperative R&D agreements with AT&T and IBM. Many other academic and industrial modeling projects also depend on support from federal agencies, such as the National Science Foundation (NSF) and the National Institute of Standards and Technology (NIST).

Two industrial-system models that are being developed at SAIC reveal the complexity and potential utility of these efforts.

Thermal spray system

A high-velocity oxygen-fuel thermal spray (HVOF TS) system uses the velocity and temperature of a supersonic jet to accelerate and heat metal or ceramic particles that subsequently coat a substrate. The high rates of deposition produced with this system make it a low-cost and versatile technology. Ceramic, composite, metal, and plastic coatings are being used to improve a material's biological, chemical, electrical, structural, thermal, and tribological properties.

In this system, a set of parameters—including particle size, gas flow, and substrate conditions—determines a coating's quality, consistency, and deposition rate. At present, these relationships are determined experimentally by plating sample after sample while varying the conditions. In other words, developing such a deposition system depends on trial and error. As a result, coating quality has not been well controlled and has been inadequate for many potential applications. Recent computer models, however, will make many new applications feasible and improve process characteristics by improving the deposition efficiency, reducing erosion of the device, lowering its energy consumption, and making the equipment more versatile and scalable.

The HVOF TS system (Figure 1a) consists of a combustion chamber with fuel- and oxidizer-injection systems, a de Laval nozzle, a barrel, particle-injection ports, and a water cooling system. High-pressure, high-temperature gas from oxygen combustion expands into the de Laval nozzle and barrel, which accelerate the gas flow to supersonic velocity. The supersonic jet flow expands into the atmosphere and quickly decays to subsonic velocity. In a TS gun, metallic particles or ceramic powder is injected into the supersonic-gas stream.

The particles are turbulently mixed, heated, accelerated, and propelled to the substrate. The system involves two-phase (gas and particle) flow with turbulence, heat transfer, chemical reactions, and supersonic–subsonic flow transition. The physical properties of the plated surface depend on the physical and chemical conditions of the impinging particles, which in turn depend on parameters including gun design, gas-jet formation, particle size, shape, material, method of injection, and position relative to substrate.

Simulation of this system requires a number of components: (1) detailed gun geometry, (2) Navier–Stokes equations for compressible flow, (3) conservation equations and constitutive relations for gas and particle phases, (4) a turbulence model, (5) a Lagrangian particle-trajectory formulation, and (6) heat and momentum transfer. Fluid velocity fluctuations caused by gas turbulence are simulated using a stochastic model, and the resulting particle motion is calculated with a Lagrangian stochastic–deterministic method. The simulation accurately models several factors: (1) gas expansion and flow in the barrel and in the free jet, (2) particle injection, (3) interaction of the particles with turbulent gas flow inside and outside the barrel, and (4) particle-wall interactions. An example of the resulting gas streams is plotted in Figure 1b.

To validate our model, the steady-state flow regime was simulated for conditions in a de Laval nozzle and gun barrel, including expansion of hot gas into the atmosphere, and compared with experimental results. The model agreed to within 10% of the calculated velocity distribution of gas on the jet centerline with measured data from W. D. Swank and his colleagues at the Idaho National Engineering Laboratory (INEL) (Figure 2a). The axial velocity distribution predicted for 40-mm particles agreed with measurements to within 5%, well within the experimental accuracy (Figure 2b).

We conducted a parametric study, including varying particle size and barrel length, to predict coating regimes that raise energy efficiency, increase coating rate, improve coating quality, reduce plating spot (the size of the jet when it reaches the substrate), and reduce equipment wear over current operating conditions. The simulations indicate that all these improvements are possible without modifying the TS equipment, and the study's optimum plating conditions are being tested at INEL through a cooperative R&D agreement with SAIC. If those experiments confirm our model, it will represent a first case in guiding TS plating conditions entirely through numerical simulations.

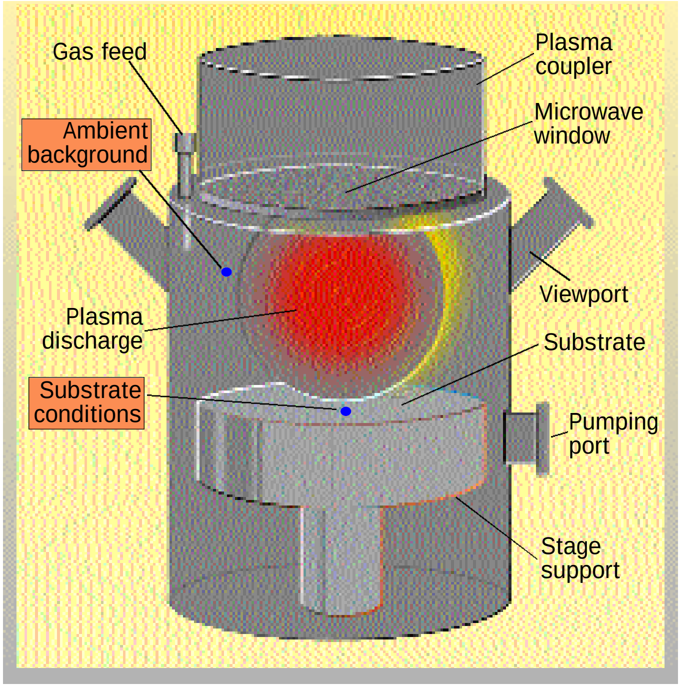

Figure 3. Schematic of a microwave-driven diamond plasma-enhanced chemical vapor deposition reactor.

PECVD

Plasma-enhanced chemical vapor deposition (PECVD) and etching are widely used in industry. The physical and chemical processes that must be modeled in these systems can be daunting. Consider a microwave-driven diamond PECVD reactor (Figure 3). A gas mixture of hydrogen and small amounts of methane and oxygen are fed through a microwave field region. A plasma is formed, and high-energy electrons dissociate some hydrogen molecules and other species. With the proper gas mixture, pressure, power input, substrate temperature, and so on, a diamond coating is deposited on the substrate. It is known empirically that a high flux of hydrogen atoms reaching the substrate is required to deposit high-quality diamond, and one goal of reactor design is producing a plasma that generates this flux uniformly over a large area.

Pressure=40 torr	Time scale (s)
Electric field establishment	10^{-9}
Electron density build-up	10^{-6}
Diffusion time	10^{-3}
System throughput time (for a diffusion reactor)	10^{0}
Thermal dissociation of hydrogen (T=3000K)	5¥10^{-2}
Atomic hydrogen recombination (T=1000K, 50% dissociated)	2¥10^{-3}
Vibrational relaxation (T=1000K)	3¥10^{-5}
Molecular ion recombination (n_e~10^{12}cm^{-3}) (eg, $e^-+H_3O^+$Æ H_2O+H)	10^{-5}
Atomic ion recombination (n_e~10^{12}cm^{-3}) (eg, e^-+H^+Æ$H_2+h\nu$)	~10^{0}
Neutral chemistry equilibrium	10^{-3}–10^{-6}

Table 1. Time scales for the components of a plasma-enhanced system.

We simulated the performance of an Applied Science and Technology, Inc. (ASTeX) microwave diamond-deposition reactor by using code modules that calculate electromagnetics, electron energy distribution (Boltzmann equation), hydrocarbon chemistry, and fluid and heat transport. The code was used to vary reactor shape and to determine the flux and uniformity of hydrogen atoms reaching the substrate versus power input and pressure. Experimental measurements by ASTeX scientists validated the results of the simulation. This simulation capability facilitated the development of a more efficient reactor with improved uniformity in large-area deposition. This success notwithstanding, the time scales of the deposition process made it difficult to extend the code's applicability without significant numerical developments.

Self-consistently following plasma generation depends on the time scales of the component processes (Table 1). Using straightforward time integration to model the longtime (steady-state) behavior of these processes is clearly impractical. However, the fast time-scale processes, such as electric-field establishment with self-consistently generated plasma and fixed-background gas, can be simulated by solving for microwave modes in the frequency domain. Then the chemistry, diffusion, and convection processes can be integrated over their much longer time scales. Unfortunately, a frequency-domain solver that includes plasma-response terms in Maxwell's equations does not lead to a converging solution using standard techniques. So we developed an approach that combines a generalized minimal-residual (GMRES) algorithm (which provides fast, guaranteed convergence) and features of a conjugate-gradient technique (which requires much less memory than GMRES).

Using this approach, we are developing a reactor model to simulate high-pressure (about 1 torr) plasma-etching reactors, which are used for removing resists with atomic oxygen and for etching silicon with atomic fluorine. We have also begun modeling low-pressure (about 1 mtorr), high plasma density reactors, in which, in addition to the elements required in high-pressure reactors, we must also model magnetic-field effects, ion transport and dynamics, and ambipolarity and sheath effects. In this reactor model, the fluid approximation for the gas breaks down and is replaced by direct-simulation Monte Carlo techniques.

Although computer simulations of industrial deposition and etching processes have shown recent progress and utility, developing comprehensive, realistic, and useful models remains a long-term, multidisciplinary program. Furthermore, model validation is difficult because most industrial reactors do not have the necessary diagnostics. Nevertheless, increasingly stringent product requirements will give computer simulation an increasing role in parameter optimization and design improvements in coming years.

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