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“Materials Processing and Manufacturing Technologies
for Diamond Substrate Multichip Modules (DSMCM)”
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Technical Summary — 1 July 1993

David S. Dandy
Department of Chemical Engineering
Colorado State University
Fort Collins, Colorado 80523

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Technical Progress — Summary

A detailed surface kinetics mechanism has been developed for the deposition of CH₃, C₂H₂, and C onto a reconstructed (100) diamond surface. The mechanism accounts for the growth of alternating dimer-trough rows. The thermophysical properties of all structures present in the mechanism have been computed using the molecular mechanics program MM3(92).

A diamond growth mechanism on the unreconstructed (100) surface has been used in a stagnation flow model to examine the effect of hydrocarbon injector location and inlet temperature on gas-phase species distributions and diamond growth rate in a DC arcjet reactor system typical of that in use at the Norton Company. It is predicted that there is an optimal injector location, dictated by operating conditions, that results in maximum concentrations of reactive growth species CH_x, and consequently, in maximum diamond growth rate.

To explore the feasibility of constructing an enclosed tank diamond reactor, a three-dimensional, non-isothermal, fluid dynamics computer code is under development. The code will be used to study mixing effectiveness at reduced pressure in enclosed (or, perfectly stirred) tank reactors. Calculations have been performed using a perfectly-stirred tank model and the unreconstructed surface kinetics mechanism.

During this period, work from this program has resulted in 1 paper being accepted for publication in *J. Appl. Phys.*, and 2 papers submitted: 1 to *J. Appl. Phys.* and 1 to *Appl. Phys. Lett.*

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Surface Chemistry

Data from AFM and STM strongly indicate that surfaces such as (100) do not remain unreconstructed, even under growth conditions. Consequently, a detailed surface kinetics mechanism has been developed in collaboration with Michael Coltrin of Sandia National Laboratories to describe the growth of diamond on a (100)-(2×1) surface. The mechanism is initiated by the abstraction of a hydrogen, and growth occurs through the adsorption of a carbon species, such as CH₃. A typical model structure for this mechanism, used to compute the thermophysical properties, is shown in Figure 1. The thermodynamic properties of all of the structures appearing in the proposed mechanism have been computed using the molecular mechanics program MM3(92). The temperature-dependent quantities predicted by MM3—enthalpy, entropy, and heat capacity—have been fit to polynomials over the temperature range $298.15 \leq T \leq 2000$ K. These data will be used in the Chemkin software to study the kinetics of the growth process.

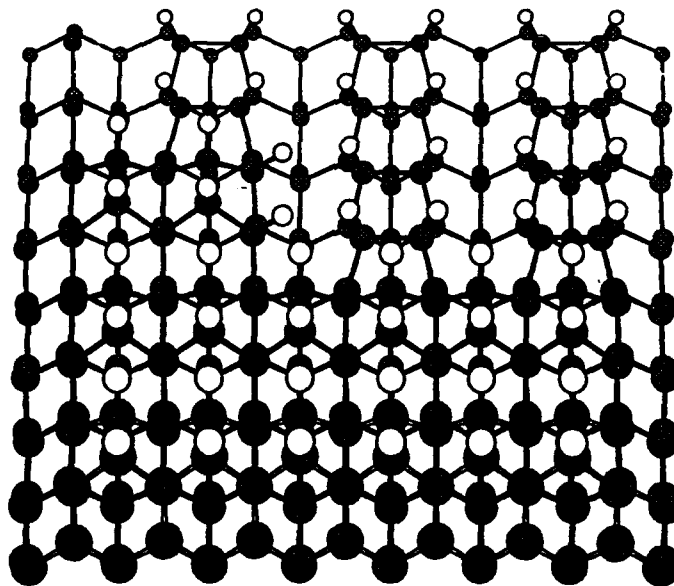


Figure 1. Model dimer structure used to compute thermophysical properties of diamond.

Carbon-bearing molecules can add to the (100)-(2×1) surface by bridging across the troughs formed by two adjacent dimer bonds, or inserting directly into a dimer bond. The model is constructed in such a way that the dimer structure repeats itself as the surface "grows," with the dimer pairs oriented 90° relative to the previous layer. There are 44 unique structures (surface species) present in the model, with over 100 reactions describing abstraction, termination, insertion, adsorption, and isomerization. The model is being tested for self-consistency and will be included in kinetics calculations in the near term.

Pedestal Reactor Calculations

Using a surface kinetics model developed by the PI and Michael Coltrin and published in *J. Appl. Phys.*, stagnation flow calculations have been carried out to study the effects of CH_4 injector location and plasma torch outlet temperature on gas-phase composition and diamond growth rate. The reason for carrying out these studies is that experiment and theory both demonstrate that under typical CVD diamond reactor operating conditions, most of the injected hydrocarbon is converted to C_2H_2 when no oxygen is present; further, theory and experiment both suggest that C_2H_2 does not appreciably contribute to diamond growth. The route to the formation of C_2H_2 , in the case of CH_4 fuel, first involves pyrolysis to CH_x species, followed by bimolecular reactions to form C_2H_6 and C_2H_4 which then convert to C_2H_2 . The question is whether this competition between chemical kinetics and transport time scales can be exploited, or at least, optimized. By varying injector location, one has some control over the residence time of the hydrocarbon mixture in the hot zone, and it may be possible to deliver more of the "desired" species (CH_x) to the substrate before they have time to convert to less desirable species, such as C_2H_2 .

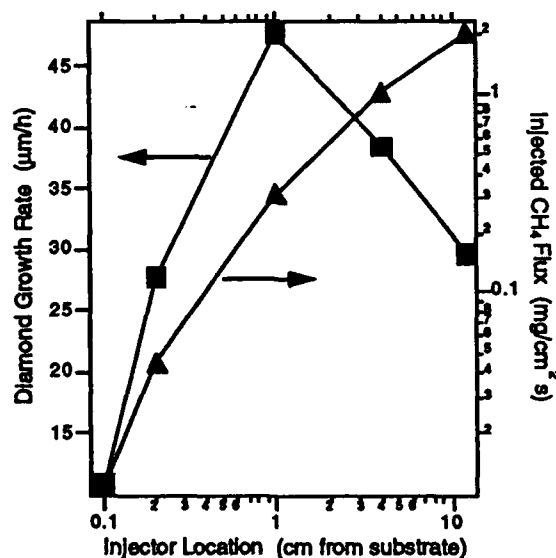


Figure 2. Relationship between predicted growth rate and hydrocarbon injector location in DC arcjet reactor.

In the stagnation flow model, the injector location was varied from 15 cm down to 0.1 cm from the substrate. It is predicted that the growth can be increased by 50%, simply by moving the injector to a region just outside of the substrate boundary-layer. The reason is

that [C] and [CH₃] at the substrate are maximized under nominal operating conditions when the injector is located 1 cm from the surface.

The effect of plasma torch exit temperature on gas-phase composition and diamond growth rate has also been studied numerically. In a plasma torch, exit temperature is a controllable quantity because is directly proportional to torch power and inversely proportional to gas flow rate. For the purposes of the calculations it was assumed that the degree of dissociation of H₂ within the torch could be specified independently of the temperature of the gas leaving the torch. Most DC plasma torches operate in a regime that yields 5–30% atomic hydrogen at the torch exit. Under these conditions, as seen in Figure 3, diamond growth rate and film quality (as measured by percent *sp*² carbon in the bulk) are both optimized at lower—less than 2000 K—torch exit temperatures.

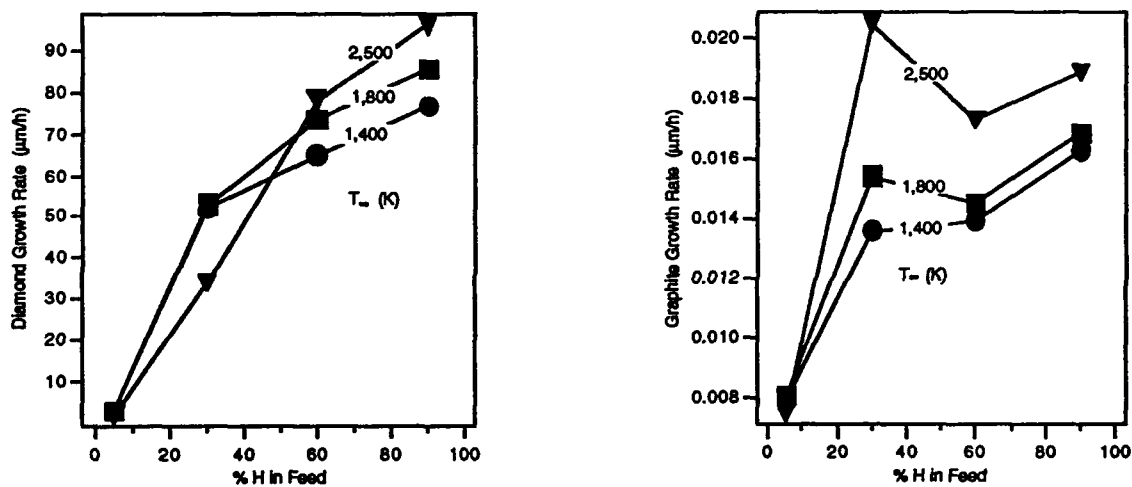


Figure 3. Predicted diamond and graphite (*sp*²) growth rates as a function of [H] at the torch exit, at different torch gas temperatures.

At lower [H]_∞ and T_{∞} , CH₃ is the predominant single-carbon species, and the conversion to C₂H₂ is relatively slow. However, when H is in great excess, the methane feed is quickly pyrolyzed to C at higher T_{∞} , and while much of this is converted to C₂H₂, a significant fraction remains as C. Therefore, it is predicted that under existing torch operating conditions, it is desirable to maintain the gas leaving the torch below 2000 K.

Stirred-Tank Calculations

Preliminary calculations have been carried out to benchmark achievable diamond growth rates in perfectly stirred tank reactor systems. The model for such a system presumes ideal mixing within the reactor volume, i.e., no spatial gradients of temperature or composition, and incorporates the unreconstructed diamond growth mechanism. By assuming a 12-inch high, six-sided (10-inches on a side) enclosed geometry, it is possible to position 6, 6-inch substrates on the side walls. For calculations purposes, this geometry fixes the reactor volume and surface-to-volume ratio. Using the same torch exit conditions (temperature and composition) as in the stagnation flow model, mass deposition rates are predicted that are up to 12 times higher than currently observed in existing DC arcjet reactors in use at the Norton Company. Pedestal reactor calculations using the same surface kinetics mechanism, yield predicted growth rates that are within 15% of those actually observed.

Coincident with these stirred-tank calculations is the development of a non-isothermal, fluid dynamics code to analyze mixing effectiveness in enclosed reactors under the low pressure conditions used in diamond growth. A central issue controlling the success of enclosed reactor geometries will be the degree to which the gas in the reactor is well-mixed. By solving the exact momentum and thermal energy equations for specific reactor geometries, we can quantitatively measure the effectiveness of the hydrodynamic mixing due to the motion of the jet issuing from a plasma gun. Initial calculations will focus on a single plasma torch jet entering along the center axis of an enclosed cylindrical reactor with cooled walls, as shown in Figure 4. Controllable parameters are jet velocity, inlet orifice diameter, reactor length scales, and exhaust port location. Later studies will consider the use of two plasma torches, located at opposite ends of a cylindrical reactor.

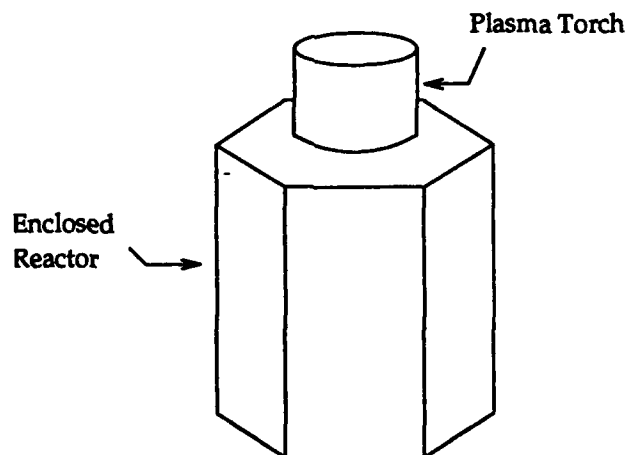


Figure 4. Schematic diagram of enclosed reactor geometry.