Thermal, Fluid, and Mass Transport Modeling of a Gas-Jet Reagent Delivery System for Laser Chemical Vapor Deposition (LCVD)

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Abstract

A gas-jet reagent delivery system for laser chemical vapor deposition (LCVD) is modeled with respect to heat transfer, fluid flow, and mass transport. A commercial package was used to model the geometry and flow field surrounding an LCVD reaction zone. The deposition temperature was analyzed for various materials and flow conditions. The forced flow environment was compared against buoyancy-driven flow, which is more typical of a statically filled chamber. A finite difference code was also developed to analyze the effect of the gas-jet on the concentration gradients above the deposition zone.

Introduction

The current study involves the development of a thermal and fluid flow model of Georgia Tech's gas-jet LCVD system, which uses a localized gas-jet to deliver reagent gases directly to the deposition zone. This system is described in detail elsewhere.[1,2] No prior research, excluding our earlier efforts,[3] has analyzed the effect of an angled gas-jet on a laser heated, non-isothermal surface.

Successful operation of an LCVD system demands that the fundamentals of the process are well understood. Since CVD is a thermally activated process, the most important process variable is temperature. In a laser-heated process such as LCVD, the temperature field is restricted to a micron scale and can vary by several hundred degrees over the diameter of the laser spot. Deposition rates typically follow an Arrhenius relationship that is exponential with respect to temperature, so it is critical to understand these two-dimensional temperature variations.

The deposition rate for a given material can be limited by either the chemical kinetics of the reaction or by diffusion and mass transport of reagent gases to and away from the deposition zone. The gas-jet reagent supply for the LCVD system was designed to remove the latter constraint by directing a high velocity stream of reagent gases at the area heated by the laser beam. However, the need and impact of such a system has yet to be determined. Therefore, a two-dimensional concentration model was developed to estimate the effects of the gas-jet with respect to local concentration variations and reaction rates.

Background

Since temperature is such an important variable in LCVD, a number of analytical and numerical attempts have been made over the years to model the temperature variations within and around the laser heated zone.[4,5] The majority assumed a Gaussian distributed laser beam and emphasized conduction as the primary heat transfer mode. Conduction has been stressed because the temperature distribution is typically calculated for an infinite or semi-infinite flat substrate. In this case, the pathways available for conduction are relatively large compared to the surface area that is available to convection and radiation losses. When more complicated geometries were considered, such as during fiber growth,[6] conduction was restricted by the small fiber diameter and a larger surface area became available for convection and radiation losses.

A few thermal models have included the effect of forced flow convection on a laser heated substrate.[3] As early as 1977, Steen[7] developed a finite element model that included a non-reacting gas jet that was coaxial with the laser beam and normal to the substrate surface. He found that forced convection and radiation heat transfer losses were indeed significant for a temperature sensitive process. More recently, Lovell[8] mapped the local heat transfer coefficient on an isothermal substrate subjected to forced flow at various angles of impingement.

Some LCVD thermal models have been extended to include the mass transport of reagent gases and the prediction of deposition rates. Kinetic models for deposition near the substrate have been proposed by Han and Jensen[9] for copper deposition, and by Mazumder and Kar[4] for titanium and titanium nitride deposition. Zhang and Faghri[10] recently proposed a three-dimensional model of the SALD process that included heat transfer, mass transport, and the loss of reagents to the deposition reaction. However, no model has addressed the viscous flow contribution of an impinging gas-jet to the mass transport of reagent gases.

Model Development

Physical System Description

Georgia Tech's LCVD system is a dual chamber design that protects the high precision stage assembly in the lower chamber from the LCVD reactions in the upper chamber. A cross section of the upper chamber is shown in Figure 1. A Gaussian distributed CO_2 laser beam enters vertically through the top of the chamber and heats a 200 µm diameter zone on the circular graphite substrate. A resistive heating element inside a ceramic housing is located just below the substrate to provide global heating. Reagent gases are delivered locally through a high velocity gas jet that impinges the substrate at a 45° angle. Patterned deposits are created by rotating and translating the substrate via the stage assembly.

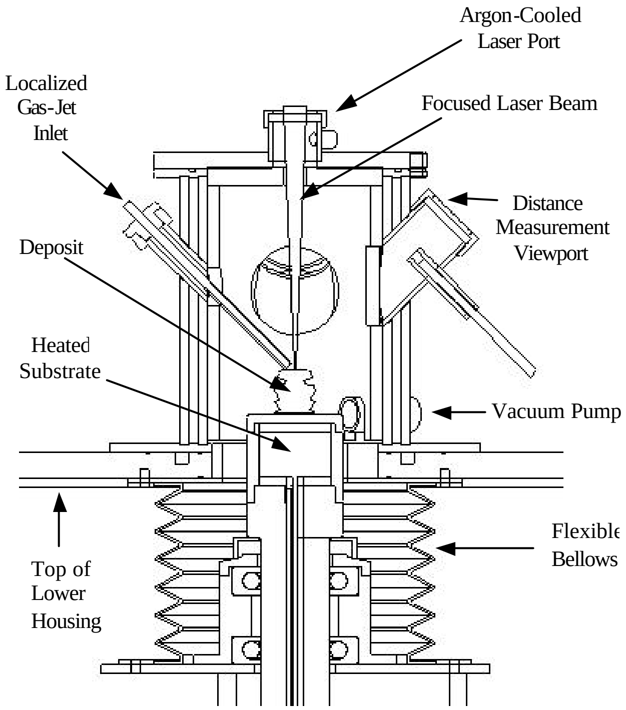

Figure 1. Cross Section of LCVD Chamber.

Thermal and Fluid Flow Models

Both two-dimensional and three-dimensional thermal and fluid flow models were developed using a commercial CFD package called FLUENT. The basic geometry and boundary conditions for each of the models are illustrated in Figures 2 and 3. For both cases, a user-defined function simulated laser heating as a Gaussian distributed energy source in the uppermost layer of elements of the substrate volume, according to Equation 1.

$$P(r) = \frac{2P_O(1-r)}{pr_O^2 t} e^{\frac{-2r^2}{r_O^2}} \qquad \textbf{(Eqn. 1)}$$

where P_o is the laser power, r is the substrate reflectivity, r_o is the nominal laser radius, t is the penetration depth, and r is the variable radius. For our setup, r_o was 100 µm, P_o varied up to 100 W, and t was typically < 5 µm.

The two dimensional model served as a platform for comparing the thermal behavior of various substrate materials when heated by a Gaussian laser beam. Figure 2 shows the basic system setup, in which the top of the graphite shaft serves as the initial substrate. For further comparisons, a given thickness of an alternate substrate material covers the top surface of the graphite substrate. The thermal and optical properties of the substrate materials were considered constant with respect to temperature, excluding thermal conductivity.

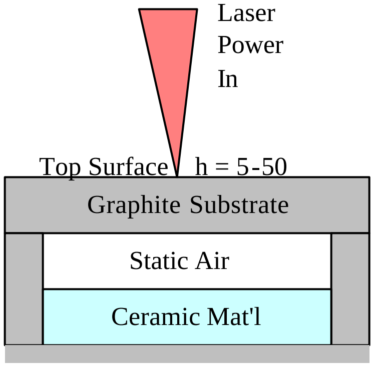

Figure 2. 2D Thermal / Fluid Model.

The two dimensional model was axisymmetric and did not account for fluid movement. Instead, the convection cooling effects associated with the gas jet were approximated by a constant heat transfer coefficient across the top surface of the substrate. The substrate was modeled as a circular piece of graphite with a diameter of 75 mm and a thickness of 6.4 mm. The side wall of the substrate holder was also composed of graphite and was 19 mm tall with a thickness of 6.4 mm. The third component of the substrate base was a ceramic heater material 13 mm thick. The bottom surface of the model was thermally insulated, while the side surfaces had a heat transfer coefficient of 5 W/m^{2}K. Radiation effects were included for each exterior surface, assuming a view factor of 1 to the chamber walls. Contact resistance was ignored.

The three-dimensional model was extended 25 mm above the graphite substrate to include the gas-jet inlet. The upper and outer boundaries of the gas volume were modeled as pressure outlets. The 1 mm diameter gas-jet was inclined at a 45° angle to the substrate with a standoff distance of 10 mm. The reagent flow was specified at the inlet as a normal velocity corresponding to mass flow rates of 0 to 5000 sccm. Since a 3D model focuses more on fluid interactions with the substrate surface, the geometry of the substrate holder was reduced to a solid graphite cylinder 25 mm thick and 75mm in diameter. This was shown to result in less than a 1% error in temperature predictions. Thermal boundary conditions matched the two dimensional case, excluding the constant heat transfer coefficient

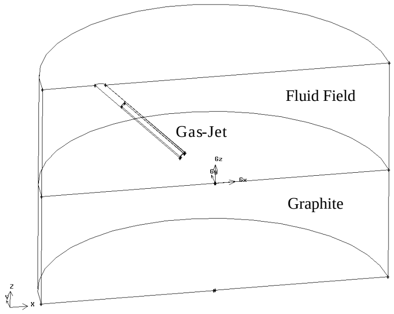

Figure 3. 3D Geometry

across the top surface of the substrate. A vertical plane of symmetry along the axis of the gas-jet was utilized, as demonstrated in Figure 3.

Transport and Concentration Gradient Model

A gas-jet delivery system is expected to aid mass transport of reagent gases to the deposition zone, thus increasing the deposition rate. In order to judge the effectiveness of such a system, a steady state, two-dimensional finite difference code has been developed. The governing equation for mass transport includes macroscopic fluid flow, diffusion, and a sink term that represents the consumption of reagents at the surface. The temperature and fluid velocity throughout the domain were accepted as input from the 3D thermal and fluid flow model previously described. The diffusion term was calculated at each node using the Chapman-Enskog method. At the surface, the sink term was nonzero and equal to kC^n, where k is the rate constant according to the Arrhenius equation, C is the local concentration, and n is the order of the reaction. After applying the boundary conditions in Figure 4, the governing equation was solved iteratively for the concentration throughout the domain. Although this model is simplistic in nature, it is a valuable qualitative tool for estimating the effects of the gas-jet on the deposition process.

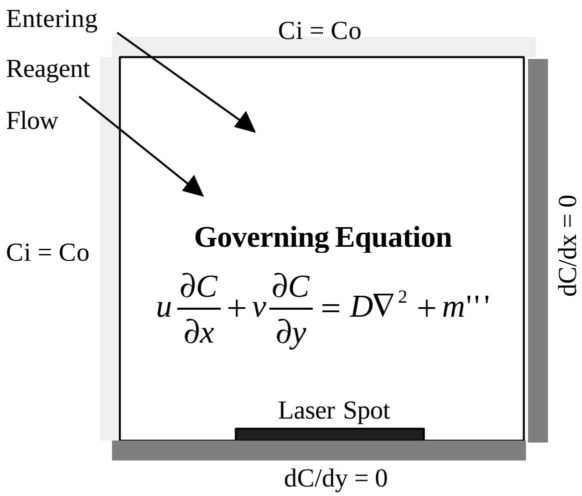

Figure 4. Concentration Model Conditions

Model Evaluation and Results

2D Thermal Model

The two-dimensional thermal model was evaluated for three different substrate materials: graphite, silicon, and tungsten. The model was empirically verified for the first two materials over a range of flow rates. Only a rough agreement was achieved at high flowrates due to exothermic reactions or poor alignment of the gas-jet. Figure 5 shows the peak temperature on each substrate as a function of laser power. Note that peak temperature increases as thermal conductivity decreases, from 108 W/mK for tungsten to 23 W/mK for silicon at 1400 K.

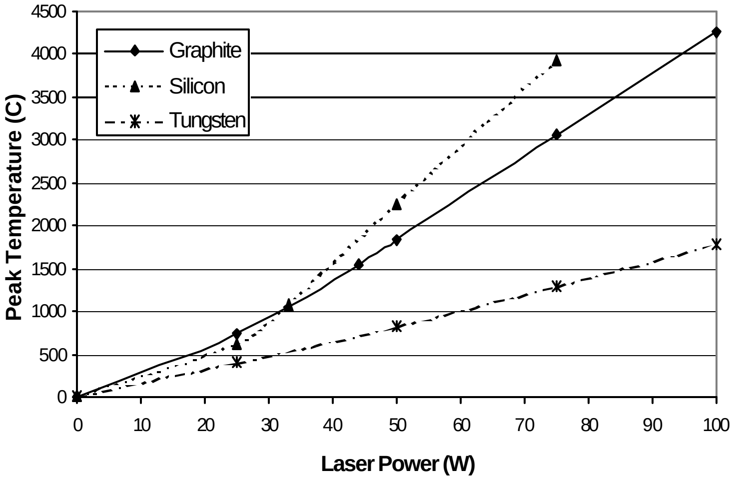

Figure 5. Substrate Peak Temperature vs. Laser Power

Not only does the peak temperature change due to the material properties, but the shape of the temperature distribution changes as well. Note in Figure 6 how the temperature profile for silicon is much more narrow than that of tungsten. For LCVD, this means that it is more difficult to achieve high resolution deposits on highly conductive substrates such as tungsten. The cooling effect of the gas-jet is approximated in Figure 7 by changes in the heat transfer coefficient. A drop of 150° C from h = 5 to 50 W/m^2K is roughly equivalent to increasing the flow rate from 100 to 1500 sccm.

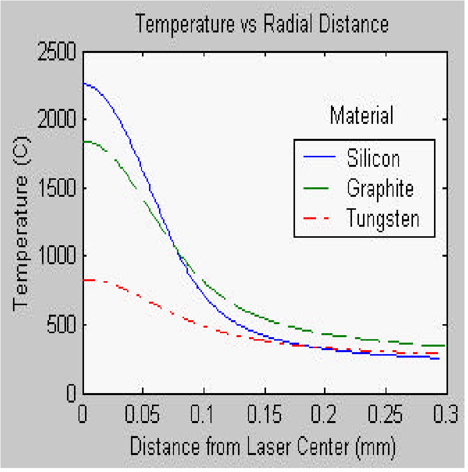

Figure 6. Temperature Distribution (50W)

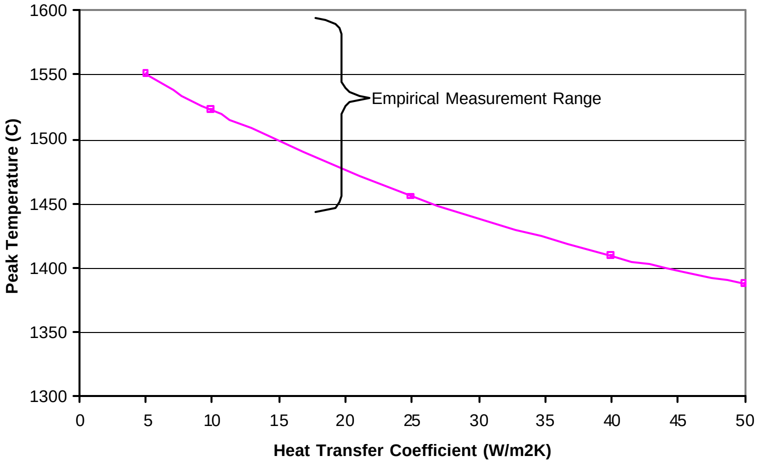

Figure 7. Graphite Temperature vs. Heat Transfer Coefficient

3D Thermal and Fluid Flow Model

The three-dimensional case models the fluid flow in the volume above the deposition zone. Substrate temperature profiles and peak temperatures correlated well with the two-dimensional models. Once again, verification experiments provided a rough guideline for peak temperatures and cooling trends. Figure 8 demonstrates a typical velocity magnitude profile for the gas-jet along the vertical symmetry plane of the model. The effects of flow rate on the temperature profiles for a graphite substrate are shown in Figure 9. The flow was composed of 80% methane and 20% hydrogen.

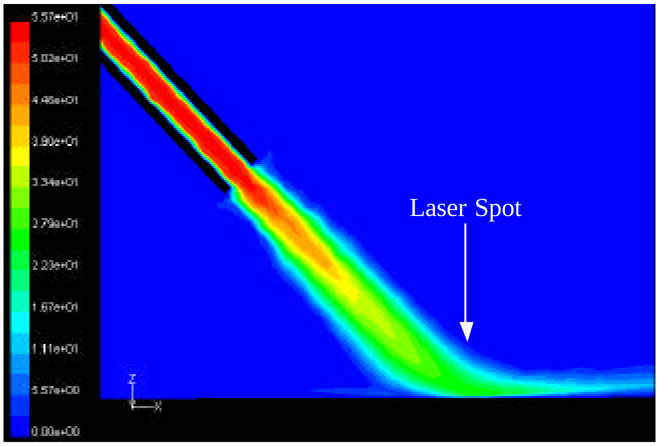

Figure 8. Velocity Magnitude (m/s) Above Substrate.

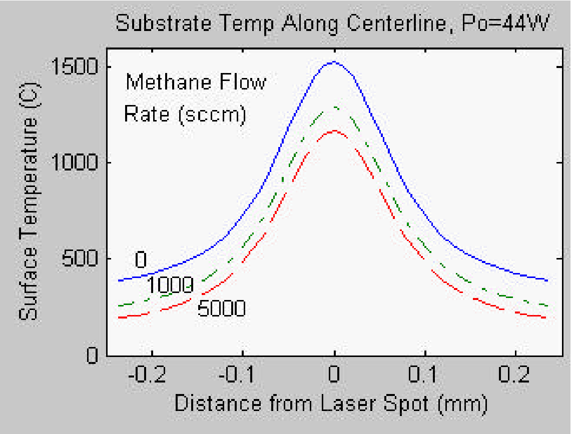

Figure 9. Temperature Profile vs Methane Flow.

Figure 10 quantitatively illustrates the velocity profiles at the center of the laser spot as a function of the vertical distance from the substrate. The height from the substrate is measured directly above the center of the laser spot in each case. Figure 10a shows that the maximum horizontal velocity imparted by the gas-jet occurs less than 400 µm from the surface. The maximum for the vertical component of flow, directed down ward onto the substrate surface, occurs at roughly twice this distance.

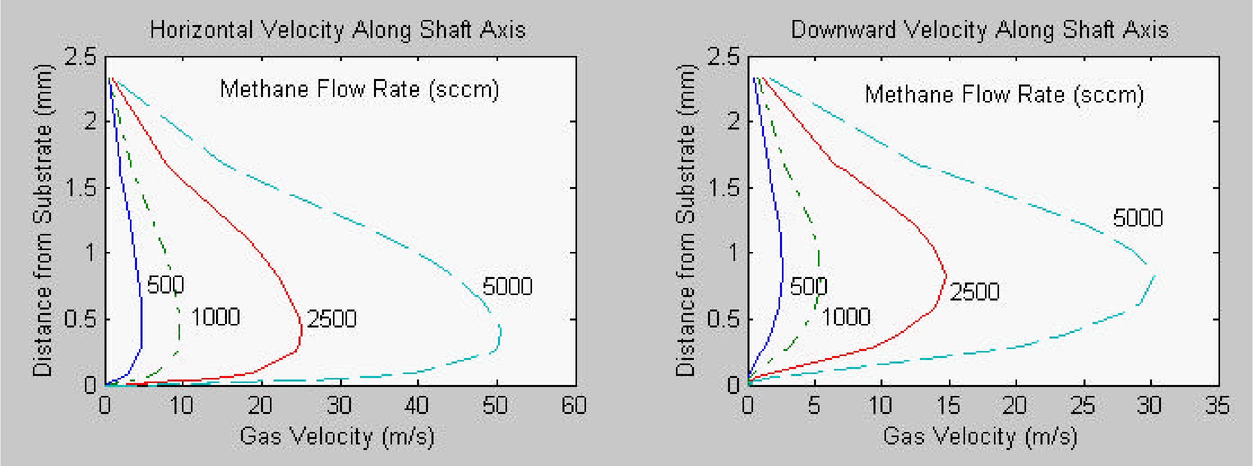

Figure 10. (a) Horizontal and (b) Vertical Velocity vs. Distance Away From Substrate Surface.

Natural Convection

A separate model was developed to investigate the effect of buoyancy-driven upward gas velocity due to density gradients induced by laser heating of the substrate surface. The surface temperature profile for the case of zero flow was applied to the base of an axisymmetric two-dimensional model. The fluid consisted of a methane / hydrogen mixture modeled as an ideal gas. Pressure outlet boundary conditions were applied at the top and side surfaces. Figure 11 shows the axial velocity resulting from buoyancy-driven flow. Notice that the maximum upward velocity also occurs around 400 µm, but is on the order of 1 mm/s -- three orders of magnitude below velocities created by the gas-jet! Although natural convection may be a concern during deposition in an otherwise static atmosphere, the buoyancy effects on the gas-jet LCVD process can be safely ignored when modeling forced flow.

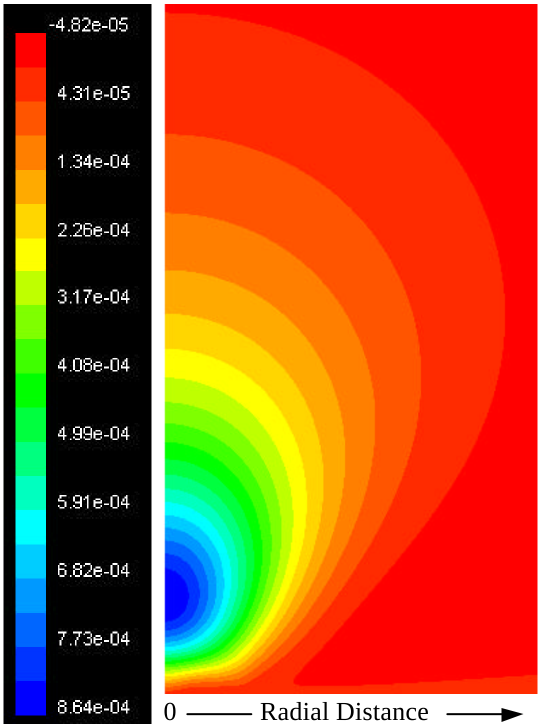

Figure 11. Natural Convection Velocity Above Substrate

Mass Transport Model

At the time of publication, the mass transport model was in the early stages of empirical verification. Preliminary results were in agreement with recent experiments involving the deposition of carbon fibers from a mixture of 80% methane and 20% hydrogen at 1 atmosphere.[11] Both the experimental data and the mass transport model indicated that fiber growth was kinetically limited at peak temperatures around 1500°C. Therefore, the model predicted minimal concentration gradients during steady state growth.

To this point, the transport model results have been very sensitive to the kinetic constants that specify the rate of consumption of reagent gases. For the results just described, the following values were used: activation energy (Q = 176 kJ/mol), pre-exponential constant (k_o = 2.6×10^{13} m/s), and reaction order (n = 3.47). Alternate values for these constants, especially the reaction order, lead to significant changes in the concentration gradients predicted by the mass transport model. The binary diffusion coefficient also impacts the model substantially. Therefore, this model may be very useful in future experiments involving the deposition of other materials or of carbon from different reagent sources.

Conclusions

An angled gas-jet has been shown to have a significant impact on both the peak temperature and temperature profile of a laser-heated substrate. The effect of natural convection on fluid flow was shown to be insignificant when modeling forced flow from a gas-jet. The maximum velocity imposed by the gas-jet occurs just 400 µm above the surface and varies proportionally to flow rate. It can be assumed that the fluid in this high velocity zone is composed of fresh reagent gases, supporting the concept that a gas-jet could aid in mass transport and diffusion. Although the effect of the gas-jet on a diffusion-limited deposition process has yet to be determined, the mass transport model has been empirically verified for a kinetic limited process and will serve as a valuable tool in future work.

Acknowledgements

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References.

1. C. Duty, D. Jean, and W. J. Lackey. "Design of a Laser CVD Rapid Prototyping System." *Ceramic Engineering and Science Proceedings,* **20** (4), 347-354, 1999.
2. D. Jean, C. Duty, B. Fuhrman, and W. J. Lackey. "Precision LCVD System Design with Real Time Process Control." *Proceedings of the Solid Freeform Fabrication Symposium*, 59-65, 1999.
3. C. Duty, B. Fuhrman, D. Jean, and W. J. Lackey. "Heat Transfer Analysis of a Gas-Jet Laser Chemical Vapor Deposition Process." *Proceedings of the Solid Freeform Fabrication Symposium*, 461-468, 2000.
4. J. Mazumder and A. Kar. *Theory and Application of Laser Chemical Vapor Deposition*, New York, Plenum Press, 1995.
5. C. Duty, D. Jean, and W. J. Lackey. "Laser Chemical Vapor Deposition: Materials, Modeling, and Process Control." Accepted to *International Materials Reviews*, January 2001.
6. D. Yu and A. Duncan. "Investigation of Induced Thermal and Fluid Transport Phenomena in Laser Assisted Chemical Vapor Deposition." *Proceedings of the ASME Heat Transfer Division,* **361** (4), 183-191, 1998.
7. W. Steen. "Surface Coating Using a Laser." *Lett Heat Mass Trans*, **4**, 167-178, 1977.
8. B. Lovell. "Local Transfer Coefficients for Impingement of an Axisymmetric Jet on an Inclined Flat Plate." *Master's Thesis*. University of Minnesota. December 1978.
9. J. Han and K. Jensen. "Combined Experimental and Modeling Studies of Laser-assisted CVD of Cu from copper(l)-hexafluoroacetylacetonate trimethylvinylsilane." *J Appl Phys,* **75** (4), 2240-2250, 1994.
10. Y. Zhang and A. Faghri. "Thermal Modeling of Selective Area Laser Deposition of Titanium Nitride on a Finite Slab with Stationary and Moving Laser Beams." *Int J Heat Mass Tran*, **43**, 3835-3846, 2000.
11. D. Jean. "Design and Operation of an Advanced Laser Chemical Vapor Deposition System with On-Line Control." *Ph.D. Dissertation*. Georgia Tech. June 2001.