

Multi-material and Advanced Geometry Deposition via Laser Chemical Vapor Deposition

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Abstract

Laser Chemical Vapor Deposition (LCVD) as a manufacturing process holds the potential to build compositionally and geometrically unique objects. Georgia Tech's LCVD system has been used in the past to create three-dimensional and laminate structures out of carbon. Recently molybdenum and boron nitride were successfully deposited and upgrades to the system have allowed for higher spatial resolutions and more varied geometric capabilities. Upgrades include the addition of a fourth linear stage and implementation of an argon ion laser. Detailed thermal and fluid modeling have provided more insight as to the important parameters and characteristics of the LCVD process.

Introduction

Laser Chemical Vapor Deposition (LCVD) is a novel process, which utilizes the properties and technique of Chemical Vapor Deposition (CVD) on a very small-localized basis for the creation of freeform parts.^{1,2} CVD utilizes reactive reagents and global heating to initiate the necessary chemical reactions for obtaining the desired deposit. The energy is typically supplied from a large heating element surrounding the reaction chamber. For this reason CVD has traditionally been used as a coating technology as opposed to a method of making freeform parts. LCVD replaces the global heater with a laser such that only the desired region is heated and therefore deposition occurs locally as shown in Figure 1. Like CVD, LCVD is used mainly to produce ceramics and metals, including many exotic materials.

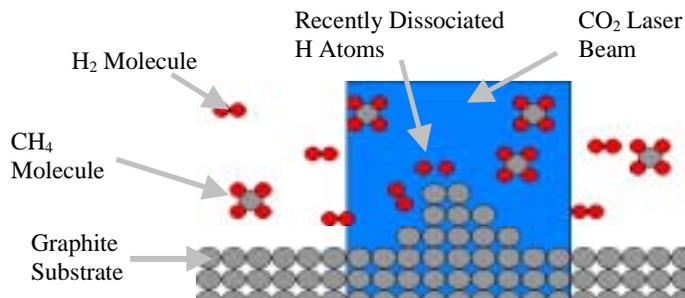


Figure 1. Schematic of LCVD production of carbon using methane and hydrogen.

Georgia Tech's LCVD system was designed to be an alternative prototyping and/or manufacturing system for parts that needed to be made of uncommon materials in specific geometries or parts that were needed in final shape after manufacture with minimal or no post processing. The system is powered by a 100 W CO₂ laser which is optically delivered by means of stationary mirrors inside a sealed reaction chamber. As the location of the laser spot is fixed within the chamber, stages are used to move the substrate, and thus the region on the substrate where the reaction is going to occur. The power of the laser can be controlled using an automatic control system monitored by a thermal imaging camera; this allows for effective controlling of temperature during the reaction. In addition to thermal control the other novel feature of our system is that it has a reagent jet that can be used to deliver fresh reagents to the reaction zone. Recently several upgrades have been made to the system to enhance our ability to make more varied geometries as well as at a higher resolution.

LCVD System Enhancements

The most significant and promising upgrade made to Georgia Tech's LCVD system has been the addition of a secondary laser, an argon ion laser. One of the greatest advantages of this laser over the CO₂ laser that is currently used is that the spot size in the reaction chamber is 10 μm in diameter as opposed to the CO₂ laser, which is 200 μm .³ Due to the larger wavelength of the infrared light emitted by the CO₂ laser, the beam can not be reduced any smaller than it's current spot size. Since the Ar⁺ falls within the visible spectrum ($\lambda=488\text{nm}$) it is possible to bring the base spot size down much smaller using standard diverging converging optics. Taking into account the power of each laser, the Ar⁺ laser should be able to produce approximately 60 kW/mm², or 20 times the power density of the CO₂ laser. Additionally the laser and optics systems were designed such that the laser can enter horizontally or vertically into the chamber. In the horizontal configuration the spot size is slightly bigger at 54 μm because of space constraints on the optics setup, while this spot is bigger than from the vertical configuration the power density is still close to that we normally use for deposition. The optics setup for the laser is also independent of that of the CO₂ laser so they can be used simultaneously. As can be seen in Figure 2 the top entry port was forced to be put on at an angle of $\sim 40^\circ$ with respect to the vertical path of the CO₂ laser so that it would not only fit with the existing hardware but also line up the spot with that of the CO₂ laser as well.

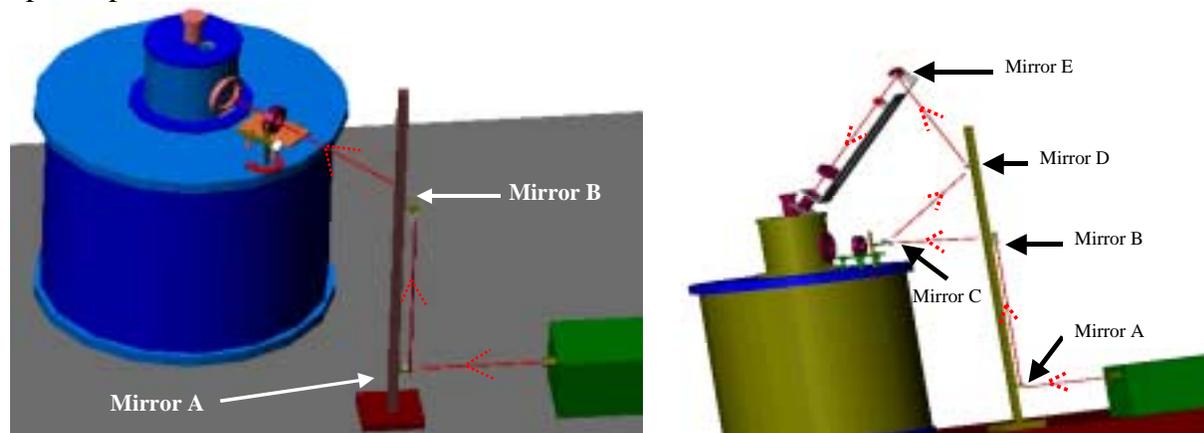


Figure 2. Models of laser entry into the reaction chamber.

In addition to the new laser, work is currently being done to add another axis of freedom to our system, a fourth linear stage. Currently the way the reactor is setup, the substrate can be rotated and translated in one horizontal direction and in the vertical direction. The new stage will allow for motion perpendicular to the current horizontal movement axis. This will also be aligned to the horizontal laser entry port such that deposition can occur from the side at varying distances from the substrate.



Figure 3. Current 3-stage configuration.

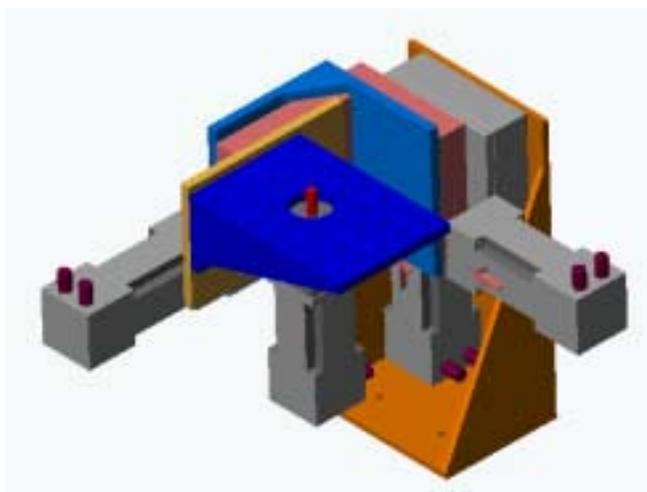


Figure 4. New 4-stage subsystem.

Modeling Efforts

Several CFD models were created to model the effect of the Ar^+ laser heating a substrate from the side port of the system. The most significant concern was that unlike the previous work done by Duty whose models represented vertical laser entry with a horizontal substrate, the Ar^+ laser will enter from the side and strike a vertical target.^{4,5} The effects of convection, both natural and forced from the gas jet reagent delivery system, need to be known such that the rate of heating and thus temperature can be determined. It was previously determined during these simulations that there was no significant effect from convection.^{5,6} The temperature distributions provided by these models should yield the information necessary to determine what materials may be deposited with the laser. Two different models were created, one utilizing two-dimensional geometry and an estimation factor for the gas jet, and the other was created in three dimensions with actual mass flow representing the gas jet.

For the two-dimensional model, the heat transfer coefficient for the substrate was varied to simulate the reagent gases flowing over the reaction zone. A model similar to this was previously used and validated by Duty for his work in dealing with the CO_2 laser and horizontal substrate. One of the most serious problems that have been found in modeling these reactions is the very small scale of the reaction zone. As shown in Figure 5, the element size is very fine ($1 \mu\text{m}$) near the center of the laser spot. As a result of the extremely small mesh size symmetry was used to try and reduce the amount of area that needed to be modeled. The results of the

simulation showed that at the laser spot, 2390 K (Figure 6) could be reached which is well above the necessary temperatures needed to initiate the deposition of carbon.

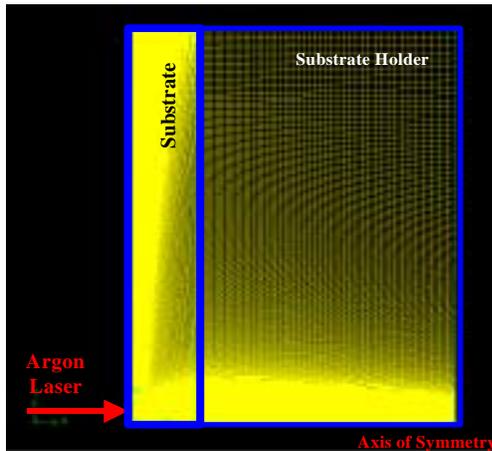


Figure 5. 2D model of elemental grid.

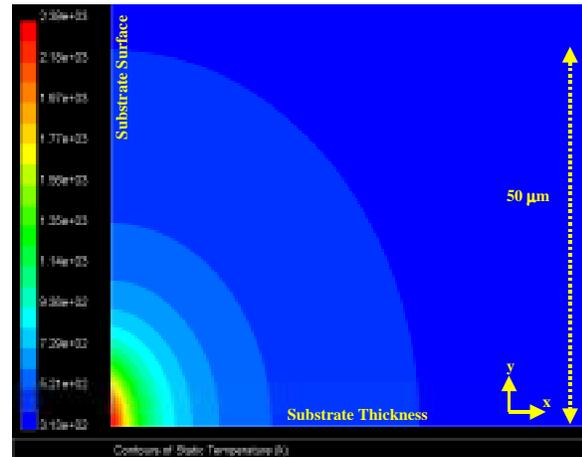


Figure 6. Temperature profile of substrate under 5 W of laser power.

In addition to the two-dimensional model a three-dimensional model was also created to better simulate the effects of the angled gas jet pointing on the substrate. Again Fluent was used but in addition to the more complex geometry, the actual mass transport was modeled. Again the use of symmetry was utilized to minimize the amount of space that had to be modeled. Figure 7 displays the geometry of the model used. Note that each rectangle on the grid where the gas jet enters the reaction zone is programmed to represent the conditions of the flow at that point. The simulation results (Figure 8) indicated a maximum temperature of approximately 2250 K, which is not far from the value of 2390 K discussed earlier. Additionally, both models had very similar temperature gradients, 40 K/ μm as opposed to 37 K/ μm in the 2D case. These results indicate that deposition should be possible. Additionally it proves that as for the overhead laser and horizontal substrate, convection is not a significant factor in the LCVD process.

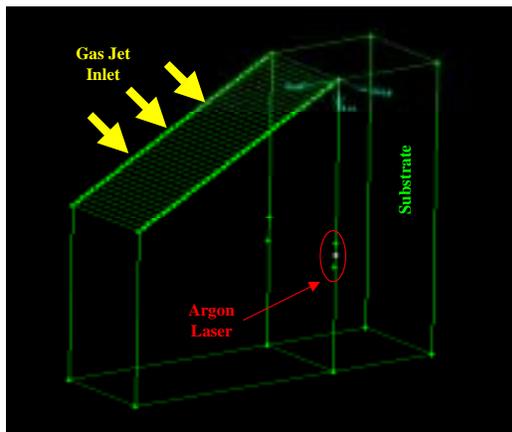


Figure 7. 3D model setup for simulation under Fluent.

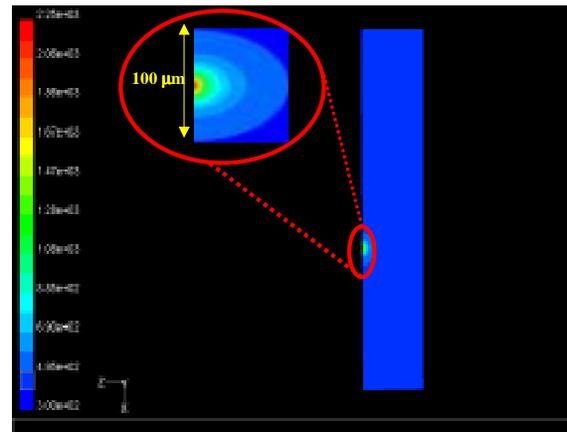


Figure 8. Results from 3D simulation of 5 W of Ar^+ laser power on graphite.

Multi-material Deposition

Georgia Tech's LCVD system has been used primarily to deposit carbon thus far, but advances in the control of the system and our knowledge of LCVD have allowed the deposition of other materials. These include boron nitride and molybdenum.⁵ Boron nitride and molybdenum are important for our work on building a thermionic emitter, which requires alternating layers of both of these materials on a tungsten substrate. As can be seen from Figure 9, the additional stage and finer resolution laser will be important in this project.

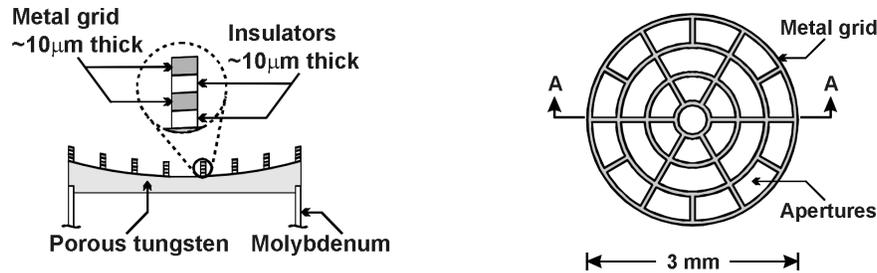


Figure 9. Schematic of a thermionic emitter to be produced by LCVD.

Boron nitride was deposited using borazine and nitrogen on alumina, graphite and tungsten substrates. Figure 10 shows one of the deposits of boron nitride on alumina, and its EDS spectrum taken in the SEM. Molybdenum deposits were made with molybdenum pentachloride and hydrogen. The substrates used were also alumina, graphite, and tungsten; Figure 11 shows one of the better coatings of molybdenum on alumina.

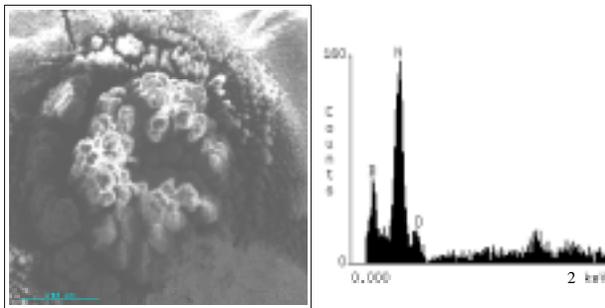


Figure 10. BN deposit on Al_2O_3 .

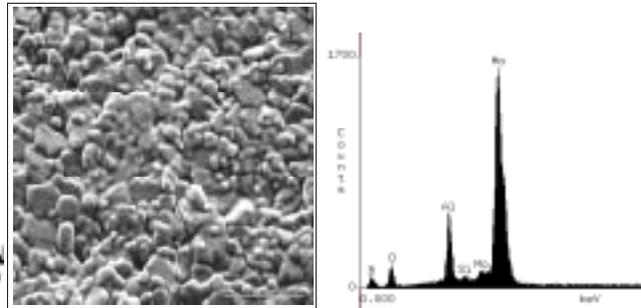


Figure 11. Mo deposit on Al_2O_3 .

Additionally the system is now capable of depositing carbon from a variety of reagents.⁷ It has been found that different reagents can produce carbon deposits with different growth and surface characteristics. Some of this work is currently being pursued to try and determine the characteristics of each combination and their potential applications.

Acknowledgements

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