

Precision Carbon Deposition Using Pyrolytic Laser Chemical Vapor Deposition (LCVD)

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Abstract

Laser Chemical Vapor Deposition (LCVD) can be used to rapid prototype many different metals and ceramics. The spatial resolution is potentially very fine, depending on the accuracy of stage or laser movement, and the size of the laser spot used for the localized heating. This paper describes a set of experiments performed using an LCVD system powered with a 100 Watt CO₂ laser. The laser was focussed to 200 μm onto a graphite or Grafoil substrate to deposit patterns of pyrolytic carbon or carbon nanotubes. The morphologies of the carbon deposits were studied while varying laser power, reagent concentration, scanning speeds and scanning patterns.

Introduction

Solid freeform fabrication (SFF) from the gas phase holds great promise as an extremely flexible fabrication technique applicable to high precision small parts. One of these fabrication techniques is pyrolytic Laser Chemical Vapor Deposition (LCVD) which uses gaseous reactants combined with the heat from a laser to selectively deposit solid material. The resolution of the deposit is on the order of the laser spot size, which can be 1 μm or smaller for visible and UV lasers. Depending on the gases present at the heated reactive zone, many different metals and ceramics can be deposited, including the potential for composites and functionally graded materials.

LCVD was originally developed to enhance the CVD process. Fiber growth became an application for LCVD beginning in the 1970's.¹ Wallenberger and Nordine performed several experiments growing fibers of B, C, Si, SiC, SiN, TiC, W, and Ge.²⁻⁴ They reported growth rates of up to 1.1 mm/s. Multiple fibers can be grown together to form structures and lattices. Micro-springs can be made by rotating and translating the substrate so that the fibers grow in a helical fashion. In 1991, Westberg *et al.*^{5,6} fabricated a boron spring 2 mm high and 200 μm wide with three turns over its length. Maxwell *et al.* formed micro-solenoids and micro-springs from C, W, and TiC.⁷⁻⁹ The fibers were as small as 5 μm , and growth rates greater than 12 cm/s were achieved for high pressure (11 bar) deposition.

Although advances have been made in the areas of fiber growth and building structures from fibers, there continues to be difficulty in depositing lines directly onto a substrate.¹⁰ Nucleation rates are very unpredictable, leading to either no deposit or uncontrollably fast

deposition. Feedback techniques are needed to control the LCVD process, such as the CCD camera used to successfully grow fibers in this study.

Physical System Description

The LCVD system consists of a CO₂ laser focused to a spot of 200 μm onto a moveable substrate (Figure 1).^{11,12} The substrate's position is computer controlled using one vertical stage, one horizontal stage, and one rotational stage. The substrate resides in a stainless steel chamber that is filled with reagent gas, while the stages are housed in a larger chamber below the substrate. A flexible bellows separates the two chambers to protect the stages from the reagent gases while allowing complete substrate motion. The reagent gases can be introduced to the chamber through a 1/16" diameter nozzle, which is pointed at the laser spot. The nozzle provides higher velocity gas flow for increased diffusion when compared to a statically filled chamber. The nozzle also decreases the residence time of the reacting gas, which may inhibit deposition in cases where the gases require a longer residence time in order to react. The local gas composition can be varied by changing the gases in the nozzle, without changing the gas composition in the entire reaction chamber. This allows for quick local changes in gas concentration, which can be useful when small variations are needed.

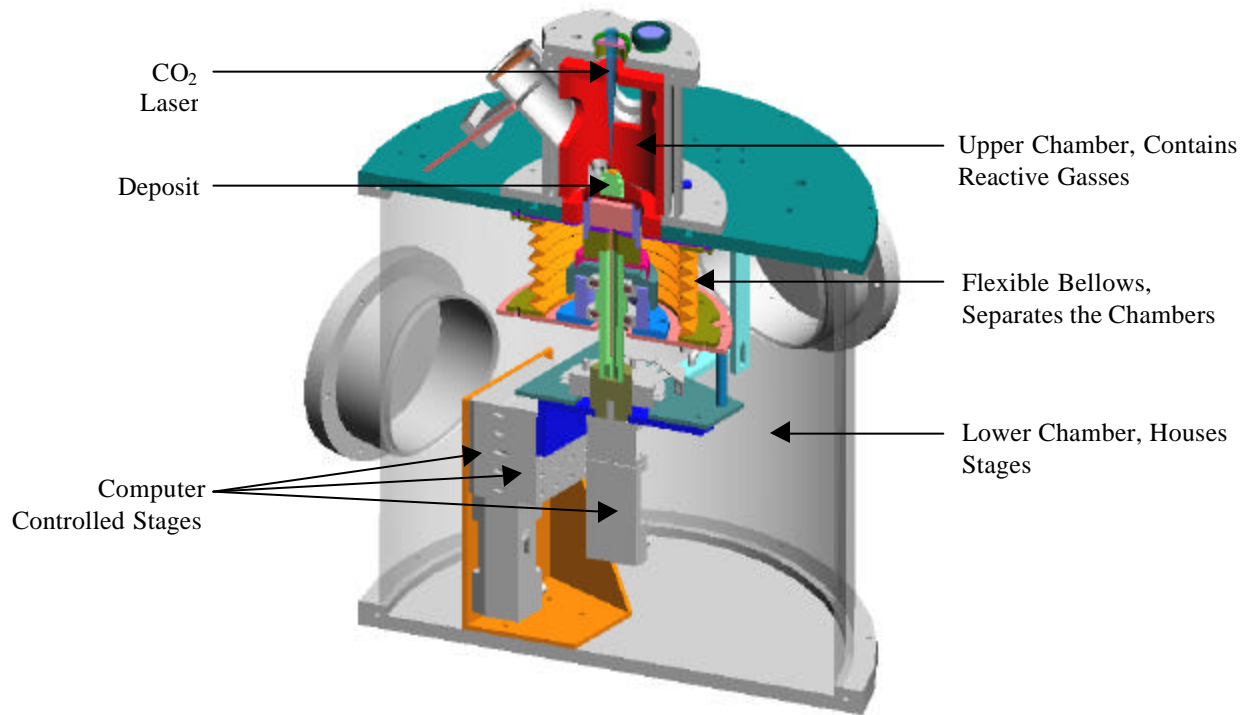


Figure 1. CAD model of the LCVD system, section view.
The upper chamber is 20 cm tall and 15 cm in diameter.

A two color optical pyrometer was originally installed in the system to measure the laser spot's temperature, but it did not have the resolution needed to measure the 200 μm laser spot. A CCD camera is used to monitor the deposition area. The CO₂ laser emits radiation at 10.6 μm

while the CCD camera records visible and some infrared radiation, up to approximately 1.0 μm . The radiation recorded by the camera is emitted by the substrate due to its high temperature, induced by the incident CO_2 laser. The intensity of light recorded by the CCD camera is used to have an approximate indication of temperature during deposition. The size of the bright circle recorded by the CCD camera indicates the size of the heated fiber tip during deposition.

Carbon Deposition on Graphite

Carbon was chosen to be the first material deposited by the LCVD system. The reagents used to deposit carbon are non-toxic, and the deposit can withstand high temperatures that may be encountered during processing. These experiments used a mixture of methane and hydrogen to deposit carbon. The hydrogen was used to prevent the formation of soot, which can occur at high methane concentrations. Graphite was used as the substrate in these experiments, mainly due to its ability to withstand high temperatures. The goal of these experiments was predictable and controlled deposition. Both fibers and lines were attempted, and the fibers were more successful.

Figure 2 shows an attempt to deposit a line of carbon on a graphite substrate. The laser was scanned at a constant velocity of 8.5 $\mu\text{m}/\text{s}$ and a constant power of 80 W. The spot size was 200 μm , resulting in a power density of 2546 W/mm^2 . The line was initially flat-topped with well-defined sides. Its width is approximately 120 μm , and its height is 20 μm . As the line was deposited, heat built up in the substrate and the reagents absorbed more energy, increasing the reaction rate. Once the deposit reached a certain height above the substrate, uncontrolled growth occurred, resulting in the large spherical structure with the cauliflower texture. The explosive growth also produced soot that can be seen around the base of the sphere. Even though the laser power and the scanning speed were constant, the deposition was far from uniform. The laser power needs to be reduced as the deposit grows to achieve uniform deposition and to prevent uncontrollably fast growth.

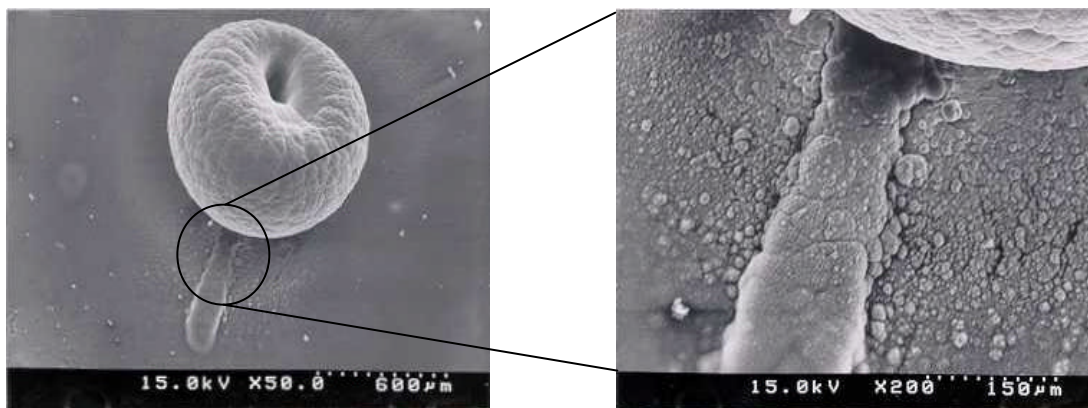


Figure 2. Carbon deposited on a graphite substrate, using 80 Watts of power focussed to 200 μm , and scanning at 8.5 $\mu\text{m}/\text{s}$. The reagent concentration was 75% methane and 25% hydrogen at atmospheric pressure.

Figure 3 shows two structures grown under identical conditions. The base of the larger structure is approximately 200 μm , allowing it to overhang the edge of the graphite substrate. The exposure time for each growth was 90 seconds, and the laser power remained constant at 68 W during the growth. This power was needed to nucleate the growth, but it proved to be too high for controlled growth after nucleation. The larger sphere has the cauliflower texture indicative of fast growth, and soot is present around its base and also coats the smaller sphere. Although these structures were grown under identical conditions, they vary greatly in size. Since the larger structure was near the edge of the substrate, less heat was conducted away resulting in higher temperatures and a faster reaction rate. This shows the strong dependence of LCVD processing on substrate geometry. For accurate predictable growth on varied substrates, there needs to be either extensive modeling or reliable feedback.

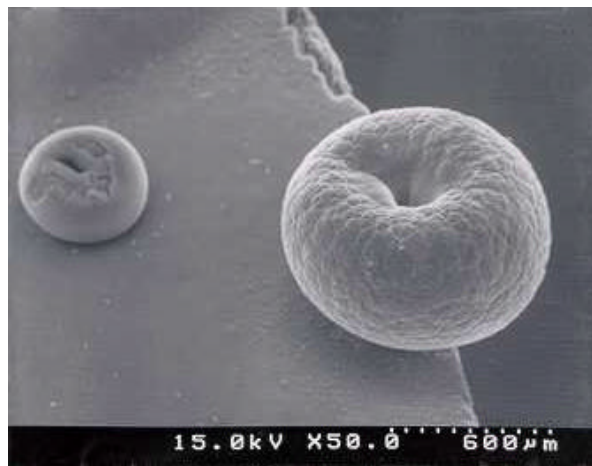


Figure 3. Both structures were deposited at 68 W of power in a static atmosphere of 75% methane and 25% hydrogen at atmospheric pressure.

The LCVD processing was monitored with a CCD camera throughout all of the experiments. The camera was focussed at the laser spot, and it recorded the bright region that was heated by the laser spot. The diameter of this bright region correlates to the diameter of the fiber or line during growth. The laser power could be adjusted manually based on the size of the bright spot to regulate the deposit diameter during processing. This visual feedback was used for the fibers grown in Figures 4 and 5. As the spot size increased, the laser power was reduced. The discrete steps of the power reduction can be seen as concentric ridges around the fiber in Figure 4. These fibers were grown with an 80% methane and 20% hydrogen mixture at atmospheric pressure under a laser spot size of 200 μm . The fiber in Figure 4 has a height of 900 μm , while the fiber in figure 5 has a height of 1100 μm .

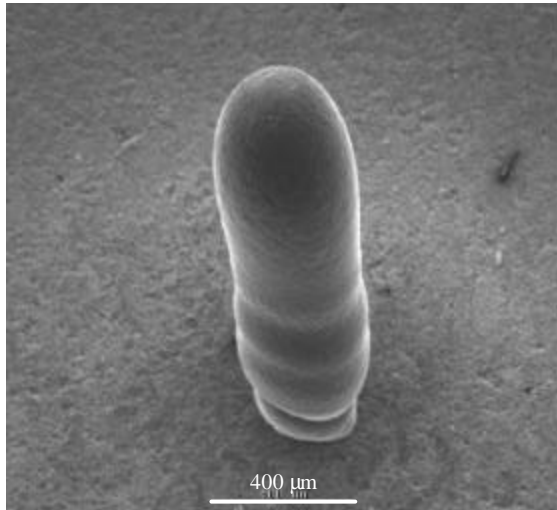


Figure 4. Carbon fiber deposited on graphite while ramping the power in 5 steps from 125 W to 42 W.

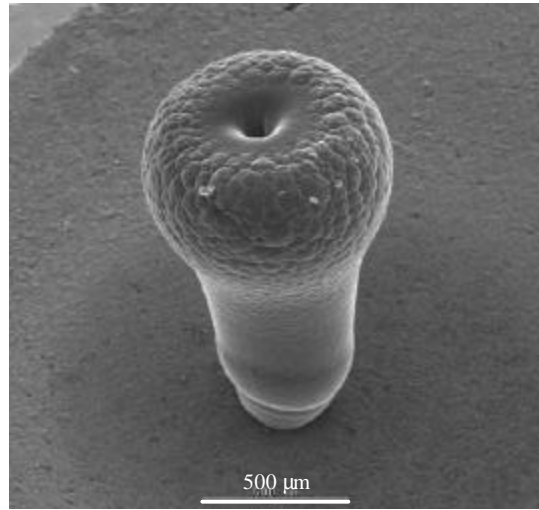


Figure 5. Carbon fiber deposited on graphite while ramping the power in 4 steps from 125 W to 60 W.

Carbon Nanotubes on Grafoil

Nanotubes are grown conventionally by depositing carbon in a CVD reactor onto a catalyzed substrate. The catalyst causes the nanotubes to grow normal to the substrate, instead of the carbon films that would be deposited without the catalyst. The growth of nanotubes in a conventional furnace requires two stages, where the concentrations of methane and hydrogen are varied. Nanotubes are grown in the first stage, where a relatively low concentration of methane is used (approximately 10% methane and 90% hydrogen). The nanotubes are thickened in the second stage at higher concentrations of methane. The high methane concentration stops the fibers from growing, while carbon is deposited on the fiber walls to make them thicker and more easily identifiable through the SEM. A growth and thickening cycle was used when depositing nanofibers in the LCVD system, but the gas concentrations were different due to variations between conventional and LCVD processing.

Nanotubes were successfully deposited onto catalyzed Grafoil, and experiments are underway to deposit nanotubes onto catalyzed silicon substrates. Figure 6 shows thickened nanofibers deposited with the LCVD system. The substrate was Grafoil, and an iron catalyst was used. The reaction chamber was first filled with 30% methane and 70% hydrogen at atmospheric pressure. The nozzle was used to deliver a 15% methane and 85% hydrogen flow of gas during in the growth cycle, and a 90/10 mixture of methane and hydrogen was delivered by the nozzle during the thickening cycle. The CO₂ laser was focused to a 200 μm spot to form the heat source for the nanotube growth, and a power density of 2865 W/mm² was achieved using 90 W of laser power. The nanotubes grew in areas adjacent to the laser spot, and not directly in the laser spot.

The nanotubes produced by the LCVD system were grown at a single location, without moving the substrate in order to simplify the process. Current research involves moving the substrate to produce a patterned array of nanofibers that will lead to the fabrication of nanofiber devices through LCVD processing.

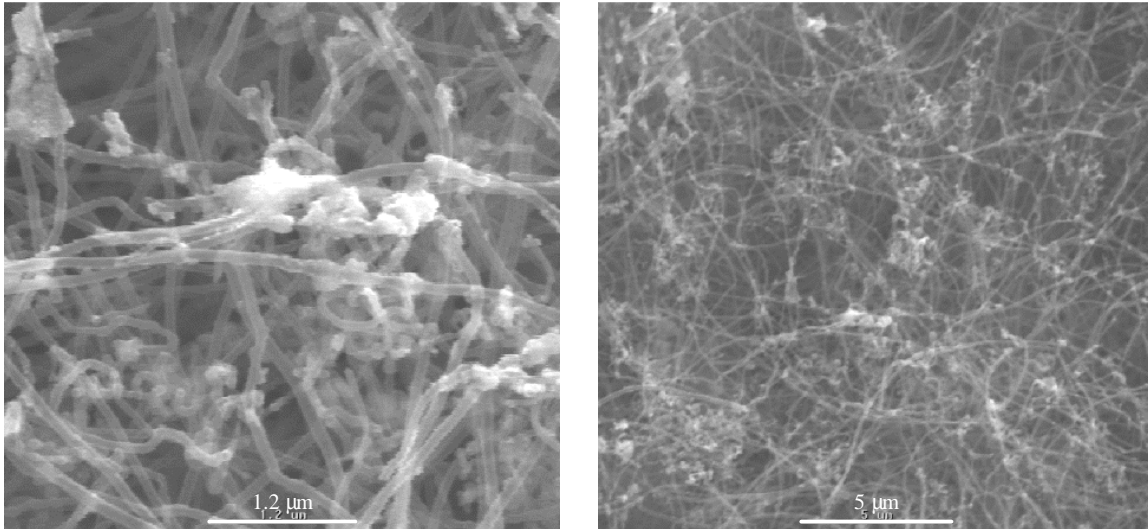


Figure 6. Nanotubes grown on Grafoil.

Discussion

The fibers in Figures 4 and 5 were grown with a large initial power, which was then ramped down as the fiber lengthened. This ramping was thought to be necessary due to the decreased thermal conductivity of the fiber. The graphite substrate requires a high power density ($\sim 3000\text{W}/\text{mm}^2$) to initiate deposition. As the fiber grows, less heat is conducted away from the fiber tip since the energy must travel down the small diameter fiber before dissipating into the substrate. The power density incident on the fiber tip must be decreased as it grows to keep the temperature constant. Although this concept of decreasing conductivity during growth does account for some of the necessary power reduction, there is another mechanism that requires a power reduction to achieve columnar fibers.

The actual deposition temperature must be reduced during the initial stages of fiber growth. The temperature to initiate fiber growth is higher than the temperature needed to lengthen an existing fiber. The reason for the high initial temperature is the shorter residence time of the reactants during the first stage of growth (approximately when the length of the fiber is on the order of its diameter). During growth of a longer fiber, the fiber is heated down a portion of its length. The reactants flow up the fiber due to convection, and are heated as they travel up the fiber to the tip. Since the reactants are heated over a longer period of time, growth is faster and a lower fiber tip temperature is needed. Only a small spot on the substrate is heated during fiber initiation, and the reactive gases may diffuse out of this heated spot before they absorb enough heat energy to react. A higher temperature is required to initiate fiber growth,

providing the heat energy to accommodate the relatively short residence time of the reactive gases.

The substrate material is limited when high temperatures are required to initiate deposition. Substrates such as alumina and silicon tended to etch or melt when subjected to high power densities. The use of global heating will reduce the need for a high initial deposition temperature, thus allowing deposition on lower melting point materials. Also, reagents that have a lower activation energy can be used to reduce the required temperature of the deposition area. Methane was used in these experiments to deposit carbon, and its residence time required for reaction is relatively long.¹³ Future experiments will employ acetylene as a reagent, which has a shorter residence time and thus will require a lower temperature to initiate fiber and line growth.

Conclusion

At constant laser power, the carbon deposit grew uncontrollably after it reached a short distance from the substrate. Higher temperatures and increased reagent heating stimulated this fast growth. Carbon fibers were successfully grown on graphite by ramping down the power as the fiber grew. The image produced by the CCD camera was used to monitor fiber diameter. The laser power was adjusted to compensate for changes in the fiber diameter as it lengthened. Future work will benefit from the implementation of an automatic system that controls the laser power to achieve desired temperatures and final part geometry.

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