Gas Phase Solid Freeform for Fabrication of Three-dimensional Ceramic Structures

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Abstract

Solid free form of ceramic materials can be achieved by deposition from the gas phase. The Selective Area Laser Deposition, or SALD, technique can be utilized to make ceramic depositions with a uniform chemical composition. In order to make all classes of ceramics, including carbides, nitrides, and oxides, selection of a precursor is an essential step. Often the correct precursor for the deposition requires a special environment, namely, one that can be uniformly heated. System design for a heated deposition chamber is discussed as well as preliminary tests of the system functionality. Silicon Carbide depositions were performed as a means of evaluating system parameters.

Ceramic materials can be made without a binder or post processing steps when the ceramic material is directly deposited into the final net shape. By using Selective Area Laser Deposition, SALD, it is possible to induce ceramic growth by controlling the movement of a laser spot across the surface of a substrate. A gaseous environment, which contains ceramic precursor gasses, will selectively decompose in the area of heat provided by the laser substrate interaction. The combination of focused laser, X-Y optics positioning stage, and vacuum chamber with a controllable environment, all controlled by a computer, create the right conditions necessary for the SALD process. This can also be applied in the Selective Area Laser Deposition Vapor Infiltration, SALDVI, mode where deposition is into a powder bed. Both deposition systems can be used for the creation of arbitrary three-dimensional layered geometries and by extension three-dimensional fill volumes for joining ceramics.[1]

Carbides and Nitrides have been deposited using this system, in particular Silicon Carbide and Silicon Nitride, with some success.[2] Silicon Carbide is used as a test case to demonstrate the efficacy of the deposition system, as all of the constituents of the final deposit, SiC, are found in Tetramethylsilane, which can be easily vaporized due to its high equilibirium vapor pressure. Other gasses are used in the SiC deposition to assist in temperature control and deposition purity. Though Tetramethylsilane is used as simple ceramic precursor, more complex precursors can also be used if the right conditions are met. Silicon Nitride for example is a product of the combination of two precursors Tetramethylsilane and Ammonia, where another level of complexity is needed and considerations such as gas ratios must be more readily considered. The system can be used to create oxides as well as nitrides and carbides, as was previously shown.[3] The production of oxides using this deposition has a unique set of challenges associated with it.

To demonstrate the potential for oxide freeform, deposition of Al_2O_3 has been explored.[4] Precursor selection is a challenge for this oxide. CVD of Al_2O_3 is often performed with conditions not suitable for the current SALD system, such as temperatures in excess of 500 C and flowing precursor gasses. In order to create Al_2O_3 and other oxides, as well as to improve

the efficiency of depositions in general, it was necessary to design a system that could be operated at an elevated temperature so higher partial pressure of the reactive gases can be used.

Certain precursors particularly metal organic precursors, which could provide the needed elemental constituents, are difficult to utilize for a number of reasons. Often, they exist as a powder, in their as received form. Powdered precursors do not usually have a high enough vapor pressure to produce the yield needed for this type of deposition. The precursor powders can be heated, but then will display unreliable vaporization characteristics.[5] In order to get past this type of problem a liquid precursor could be used but nevertheless the vapor pressure could be low with many organometallic liquids. Trimethylaluminum, is just such a precursor. Trimethylaluminum is used as the Aluminum source for the deposition of Al_2O_3; It has been used in the process of Atomic Layer Deposition but not frequently as a Laser CVD precursor.[6] To use this chemical in the SALD system with the need for higher yields in mind, it was necessary to redesign the deposition system so that operation at elevated temperatures is possible.

To Make the SALD system capable of higher temperature operation (ambient to 350 C), several design features were incorporated. The Chamber was designed to create as uniform an environment as possible. A simple flanged cylinder was chosen as the main reaction area. A series of computer controlled band heaters act to heat this chamber. The temperature of the chamber is controlled by a temperature-PID control loop operating over three distinct thermocouple-heater regions. All incoming gasses feed into a single heated manifold, also PID controlled, and the precursors can be individually heated. Seen below is an image of the deposition chamber in its current iteration.

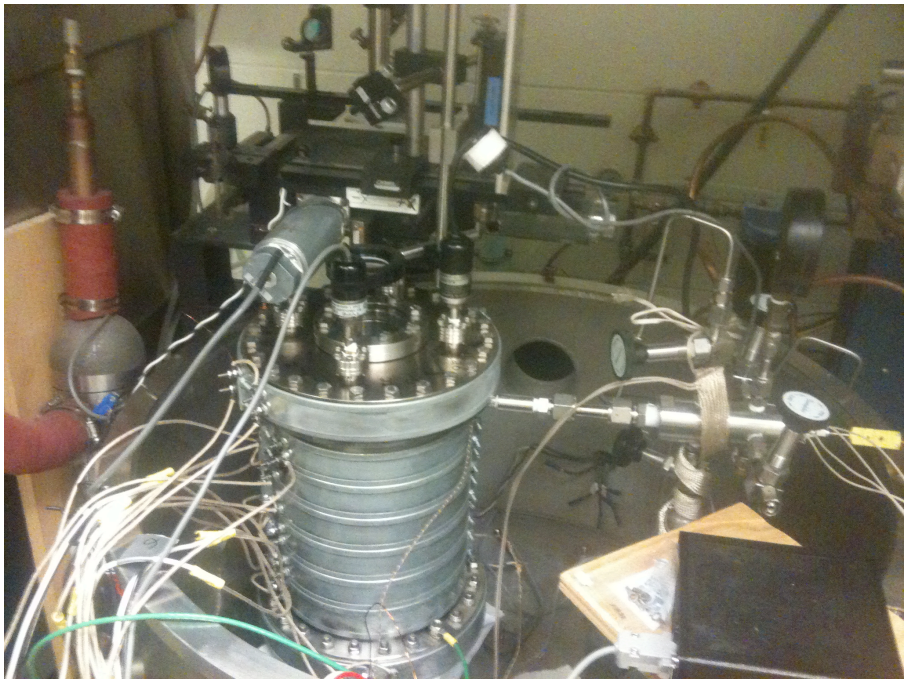

Figure 1:
Heated SALD Deposition Chamber: Pictured above are the heated chamber, X-Y positioning system and optical train, and heated precursor and gas manifold.

The primary purpose for heating the system is to allow for increased vapor pressure of the reactants and consequently a higher potential deposition yield. Some of the precursors that have been explored will not be viable for this process if they are not heated. In general, the precursors would be heated to a certain temperature to achieve a desired equilibrium vapor pressure. The gasses would then be introduced to a chamber slightly hotter than the precursors partial pressure equilibrium temperatue., so that condensation of the precursor gasses will be prevented within the deposition chamber. An example of the vapor pressure verses temperature chart of Trimethylaluminium is shown below.

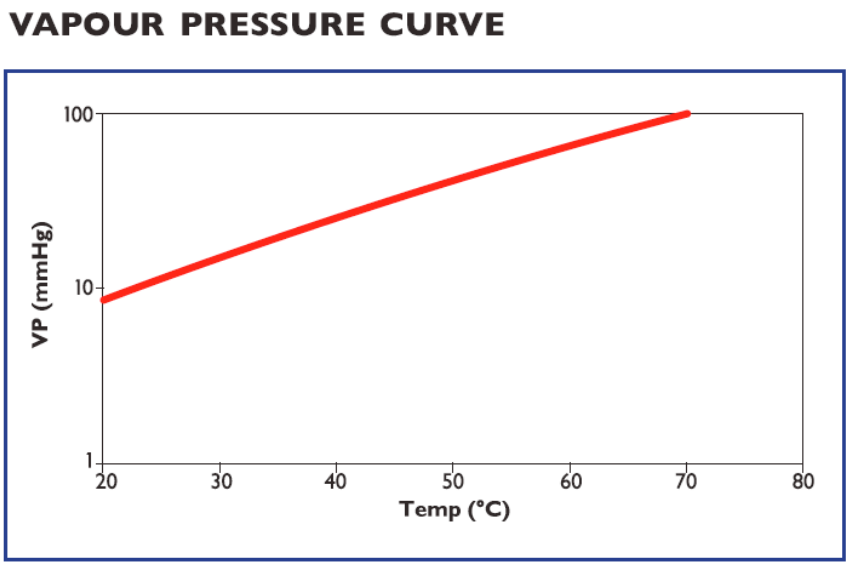

Figure 2:
Vapor Pressure Curve of Trimethylaluminum[7]: At ambient the vapor pressure is less than 10 torr which limits the deposition rate. Elevating the system temperature will greatly increase the rate of precursor influx; a vapor pressure of 100 torr at ~ 70C would be suitable for deposition.

In a similar manner to above, the vapor pressure of Tetramethylsilane can also be increased. It is not necessary to raise the temperature of TMS in order to achieve a workable vapor pressure, as the equilibrium pressure is higher than 600 torr at 20 C.[8] SiC does however make a good test of the system as it is relatively stable and not pyrophoric as TMA is.

There are several parameters that can be varied during the deposition runs. These parameters include: gas composition and mixture ratios, laser power, focus and modulation, number of passes per layer of SFF structure, temperature of the chamber, and laser scan speed. The test of the system was performed with the following parameters held constant: laser power, modulation (duty cycle), and gas concentration. The aim of the experiments was to vary several parameters and then to repeat the experiments at a series of elevated temperatures.

A laser power of 3.5 watts, CW, generated from a 1070 nm fiber laser, was used with a focused spot of 90 micron. The substrate was 3mm thick sandblasted Titanium. Reaction Gasses used were, 50 torr TMS, 300 torr Helium, and 50 torr Hydrogen. Scan Speeds of 10, 50, 250, and 1250 microns per second were used in combination with 1, 5, and 10 superimposed scans per (hypothetical) layer. The object of the tests was to vary scan speed and number of passes over the same spot, in order to understand the deposition characteristics on this substrate. This information would then be used for the construction of multiple layered arbitrary shapes of Silicon Carbide. Deposition results are summarized below.

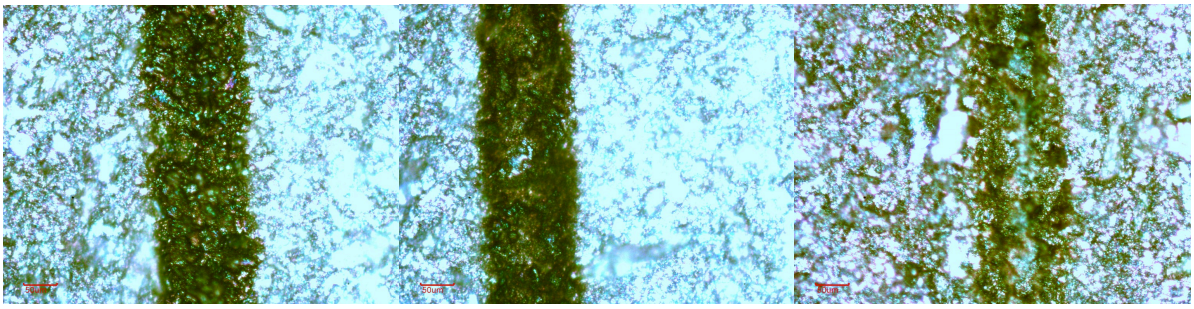

Figure 3:
Single layer deposition runs of SiC on Titanium with scan speed varying from left to right, 10, 50 and 250 microns/ second. Visible light microscopy was used with a 20X objective.

The scan speeds above resulted in very fine deposits, well bonded to the titanium substrate. The scan speed of 50 microns per second resulted in the most even deposition across the beam profile. The scan speed of 250 microns per second resulted in the thinnest deposition layer above although a speed of 1250 microns per second was also tested and resulted in an uneven and very light deposition not easily imaged by optical microscopy.

250 microns per second was chosen as the scan speed to test multiple co-spatial passes of 5 and 10 passes per line. In this case the positioning capabilities were also tested. The images below are segments of 2mm radius circles of SiC deposited onto Titanium substrates.

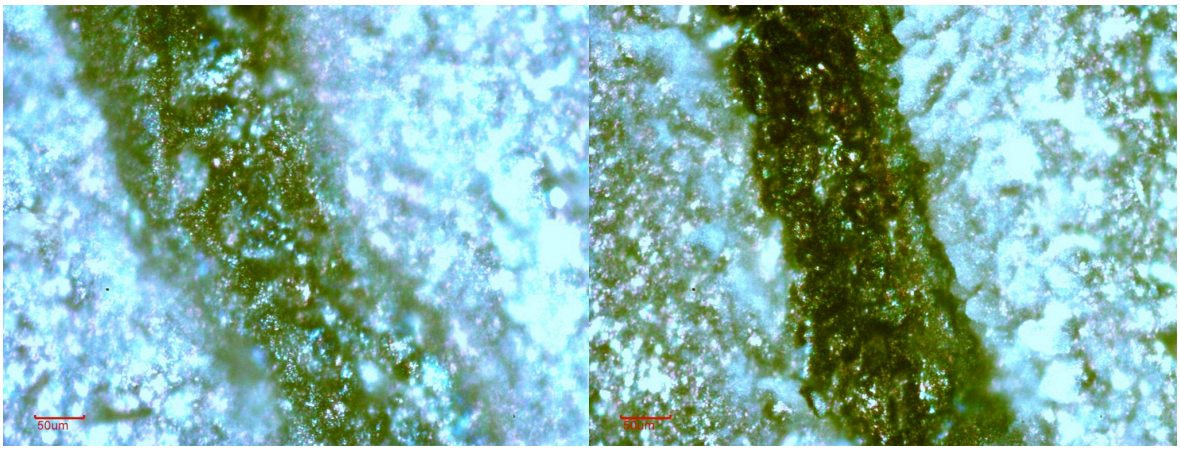

Figure 4:
Both depositions above were made with a scan speed of 250 microns per second. The left deposition was made with five consecutive passes of the laser and the right deposition was made with 10 consecutive passes.

The highest scan speed, of the three viable scan speeds, was chosen because multiple passes at the lowest scan speed resulted in runaway growth. This runaway growth resulted from excessive heating of a small protrusion, which then grew upward and away from the surface.

The test of the heated chamber showed that the chamber could be maintained at a temperature of 50 C with a variation of ±5 degrees over the different temperature zones. Equipment failure prevented the running of high temperature deposition tests in time for this paper.

A temperature controlled deposition chamber will facilitate the formation of oxides with low vapor pressure precursors. Oxides of interest are Al_2O_3, which requires special oxidizers and a metalorganic source, and hydroxyapatite, which will require two dissimilar precursors, combined to make a complex oxide with an additional outside source of oxygen. Tests of the system with SiC precursors will illustrate the potential for more novel deposits. The system will be used to achieve the freeform of ceramic materials that have not been deposited by selective laser deposition previously.

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[7] High Performance Chemicals for Advanced Semiconductor Applications, Sigma Aldrich

[8] Trimethylaluminum Trimethylaluminum