

Fabrication of Advanced Thermionic Emitters Using Laser Chemical Vapor Deposition-Rapid Prototyping

Brian T. Fuhrman, Chad E. Duty, Daniel L. Jean, W. Jack Lackey
Rapid Prototyping and Manufacturing Institute
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0405

Abstract

Laser Chemical Vapor Deposition-Rapid Prototyping (LCVD-RP) is a relatively new manufacturing process. Its capabilities are ideally suited for the manufacturing of a type of electron emitter called an integrated-grid thermionic emitter. The integrated-grid thermionic emitter is composed of wagon wheel-like structures of alternating layers of boron nitride and molybdenum on tungsten. The goal of this paper is to determine the feasibility of using LCVD-RP technology to manufacture advanced thermionic emitters.

Introduction

The purpose of this paper is to determine the feasibility of using LCVD-RP to produce a thermionic emitter used in a Pierce-type electron gun. The Pierce-type electron gun utilizes a thermionic emitter composed of wagon wheel-like grid structures of molybdenum suspended over a concave piece of barium impregnated tungsten. The performance of the electron gun is dependent on minimizing the distance between the tungsten and the molybdenum grid. Current manufacturing methods mechanically suspend the grid over the tungsten. Although this method is currently more cost-effective, it is the limiting factor for the performance of the emitter. LCVD-RP has the potential to manufacture advanced thermionic emitters by reducing the distance between the metal layers and the diameter of the emitter. However, the potentially high cost of developing and implementing this technology may not economically justify the improvements in performance.

LCVD is the process of using the thermal energy from a laser to induce a chemical reaction to occur within special reagent gases to produce a solid deposit. Depending on the reagent gases, a variety of metals and ceramics can be precisely deposited onto a substrate. Since the material is deposited on the atomic level, the deposit is fully dense and homogenous. The material properties of the deposit more closely match the theoretical bulk properties. Current metal and ceramic rapid prototyping processes, such as selective area sintering, sinter metal or ceramic powder particles together. The properties of the material are dependent on the strength of the bond between the sintered particles.

Much work has been done in the field of LCVD in the past 25 years. A wide variety of metals and ceramics such as Ag, B, Si, C, SiC, Si₃N₄, Al₂O₃, TiN, TiC, and Ni have been successfully deposited as fibers utilizing LCVD.^{1,2} In addition to fibers, several researchers have been successful in depositing materials in the form of films and lines. Mutoh *et al.*³ deposited

alternating layers (5 to 25 nm thick) of tungsten and carbon by quickly scanning a laser over a relatively large cross-section. Other researchers have been successful in the direct writing of TiN⁴, Al⁵, Au⁶, Si⁷, GaAs⁸, and Cu⁹ onto various substrates.

In the past 10 years, several researchers were successful in depositing three-dimensional structures using LCVD-RP. In 1991, Zong¹⁰ created a rectangular block of graphite. Other shapes such as a sphere, an hourglass, and a micron-sized needle were created from C, Ni, W, and Fe.^{11,12} Maxwell *et al.*^{13,14} deposited carbon in the form of helical springs. Fiber diameters of the spring as small as 5 μm and spring internal diameters as small as 60 μm were achieved. These springs were utilized for functioning microsolenoids.

LCVD-RP Thermionic Emitters

Thermionic emitters are used as the electron source inside electron guns. Devices such as television tubes, microwave emitters, oscilloscopes, and cathode ray tubes utilize an electron gun to create the picture on the screen. A thermionic emitter is composed of a piece of metal called a cathode with a metallic control grid suspended over it. Electrons are produced by the thermionic emitter by applying a high negative voltage to the cathode (generally, the cathode voltage is referenced to zero). The number of electrons that are allowed to pass are controlled by the voltage applied to the control grid. The closer the voltage on the control grid is to the cathode voltage, the greater the number of electrons are repelled back to the cathode.

The accuracy and precision of thermionic emitters is limited by current manufacturing techniques. The control grid has to be mechanically supported above the cathode by means of rods or other mechanical devices. If the grid is too close to the cathode, the heat from the cathode can warp the control grid causing imprecise operation and even a short circuit. The closer the control grid is to the cathode, the better the sensitivity of the thermionic emitter.

Fabricating an integrated grid design where the cathode and control grid are one unit is an attractive alternative. However, current manufacturing methods that would apply in this situation are limited to planar assemblies. Ohlinger¹⁵ suggested that LCVD-RP could be used to create miniature, stable, high power bonded grid emitters. He suggested that a wagon wheel-like grid structure be created on a concave tungsten substrate as illustrated in Figure 1. The grid would consist of alternating layers of boron nitride and molybdenum. Because of the properties of boron nitride, the boron nitride layers would isolate the molybdenum grid from the tungsten substrate and also prevent their distortion. By using the boron nitride layers, the grid can be physically closer to the cathode without the problems associated with previous designs.

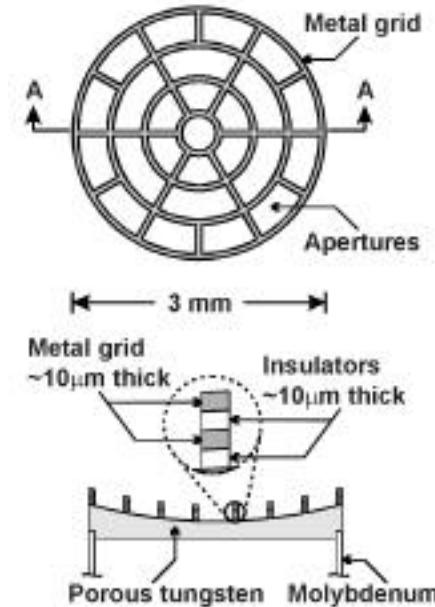


Figure 1: Thermionic emitter via LCVD-RP.¹⁵

Experimental Design

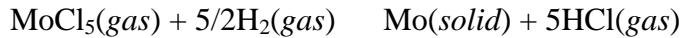
The goal of this research was to determine the feasibility of using LCVD-RP to create a thermionic emitter as illustrated in Figure 1. If alternating lines of molybdenum and boron nitride could be deposited onto a tungsten substrate, this process could be used to create a thermionic emitter. Experimentation was done on depositing boron nitride onto both tungsten sheet (99.95% pure, 0.01 inch thick) and molybdenum sheet (99.95% pure, 0.05 inch thick). To acquire the process parameters for depositing molybdenum, 0.75-inch diameter, 0.125-inch thick graphite disks (ATJ grade graphite from UCAR Carbon Company) were used as substrates.

Boron nitride can be deposited from boron trichloride, ammonia, and hydrogen via the following equation:



Hydrogen gas (H_2) was used to dilute the mixture and to react with the chloride to eliminate all of the BCl_3 (hydrogen was not included in the above chemical reaction). Because of the vapor pressure of BCl_3 , it was necessary to heat both the BCl_3 line and the other reagent line to approximately 50°C. As has been reported,¹⁶⁻¹⁸ BCl_3 and NH_3 can react at lower temperatures to produce a white powdery substance of NH_4Cl . To reduce the formation of this powder on the substrate, the substrate was globally heated to approximately 350°C. In addition, the BCl_3 and NH_3 reagents were allowed to mix approximately 15 to 30 mm from the substrate (more detail is given in the Experimental Setup section).

The deposition of molybdenum from molybdenum pentachloride and hydrogen is illustrated by the following reaction:



It was necessary to sublime MoCl_5 into a gas because it is a solid powder at room temperature and atmospheric pressure. Saeki *et al.*¹⁹ experimentally related the sublimation temperature to the partial pressure of MoCl_5 by the following equation:

$$\log(P_m) = \frac{-3504}{T} + 9.465$$

Where P_m is the partial pressure of MoCl_5 in torr and T is the sublimation temperature in Kelvin. This equation is applicable between 80 and 150°C (353 and 423 K).

Experimental Setup

The design and capabilities of the experimental system used to conduct this research have been described in detail elsewhere.^{20,21} As an overview for this paper, a brief description of the system follows. The primary components of the experimental system consists of the reaction

chamber, the laser, the reagent and vacuum lines, and the laser beam delivery system. Figure 2 is an illustration of the functions of the reaction chamber.

The equipment was actually composed of two separate chambers. The upper chamber (as illustrated in Figure 2) was the actual reaction chamber. The lower chamber was responsible for housing and protecting the three movable stages from the reagent gases (not shown). The upper chamber contained several novel features to aid in the deposition process. To improve the deposition rate, the reagent gases were delivered to the reaction zone via a jet nozzle. To reduce the deposition temperature the laser had to achieve, a resistive heater was used to globally heat the substrate. Other features included the use of a CCD camera to visually monitor the process and a distance-measuring device to measure the height of the deposit (this feature was not used for these experiments). A 100-Watt, CO₂ laser focused approximately to 200 μm, irradiated the substrate.

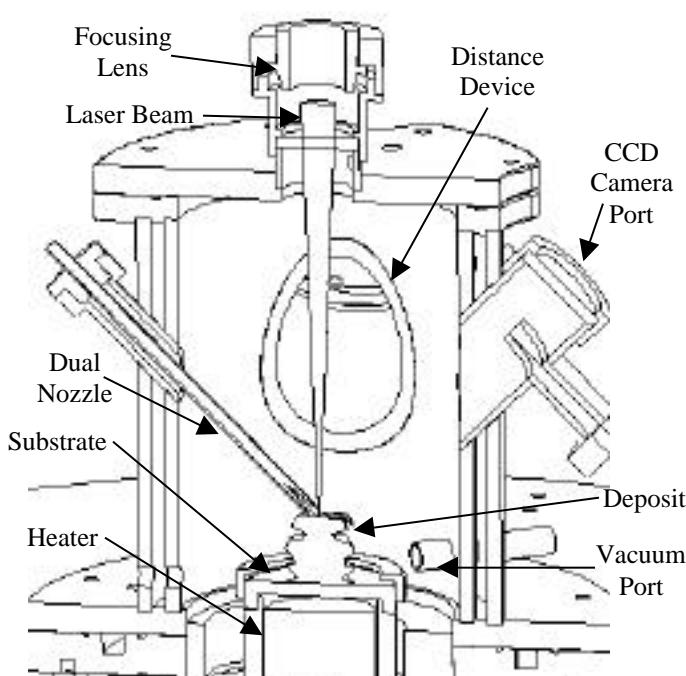


Figure 2: Schematic of LCVD-RP reaction chamber.

For the deposition of boron nitride, it was discovered that if the reagents were allowed to mix before the chamber, a white, powdery substance appeared within the chamber. Therefore, concentric nozzles with BC_l₃ in the outer nozzle and the other reagents in the inner nozzle were used to lessen the mixing distance from the substrate. The nozzle was approximately 15 mm from the surface of the substrate.

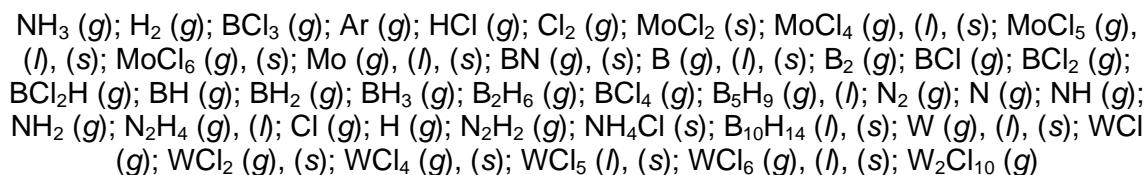
Thermodynamic Model

A thermodynamic model of the interaction between the reagents used for depositing boron nitride and the tungsten or molybdenum substrate was developed. Deposition temperatures from 300 to 1500 K, deposition pressures of 0.5 and 1.0 atmosphere, and NH₃ to BC_l₃ ratios of 1 to 5 were used as input conditions for the model. Because of the high deposition temperatures for boron nitride, there exists the possibility that the molybdenum or tungsten could have reacted with the chlorine from BC_l₃ to produce a molybdenum or tungsten chloride. After the initial experimentation, a white powdery substance that was believed to be NH₄Cl (to be discussed in further detail in the Results and Conclusions section) was deposited on the surface of the substrate. Because the majority of the substrate and surrounding chamber was close to room temperature, the thermodynamic model of the substrate was carried out at the lower temperatures to confirm the experimental results.

The computer program SOLGASMIX-PV was used to analyze the thermodynamic reactions. SOLGASMIX-PV utilizes an iterative method to determine the minimum Gibb's free energy of the mixture. The change in Gibb's free energy is related to the entropy and enthalpy of the elements and compounds by the following equation:

$$\Delta G = \Delta H - T\Delta S$$

Where G_i is the change in Gibb's free energy (kJ/mole) for the i th species, H_i is the change in enthalpy (kJ/mole) of the i th species, T is the temperature in Kelvin, and S_i is the change in entropy (kJ/mol/K) of the i th species. The calculations were dependent on the quantities of the reactants, the temperature and pressure of the system, and the respective enthalpy and entropy of the possible products (which can be solid, liquid, or gas). The following is a list of the possible byproducts considered for this model:



Where "g" is gas, "l" is liquid, and "s" is solid. All of the thermodynamic data used in the model were taken from the JANAF thermochemical tables.²²

The SOLGASMIX-PV program calculated that no chloride byproducts were formed at temperatures above 600 K. Confirming the experimental results, the computer program calculated that NH_4Cl formed in addition to solid BN at reaction temperatures from 300 to 600 K. Figure 3 is a graph of the moles of NH_4Cl formed versus the deposition temperature. Each line represents the amount of NH_3 used in the thermodynamic calculations. The calculations indicated that if the NH_3 to BCl_3 ratio was one to one, only a small fraction of NH_4Cl is formed. Each additional mole of NH_3 used resulted in the formation of an increasingly greater quantity of NH_4Cl .

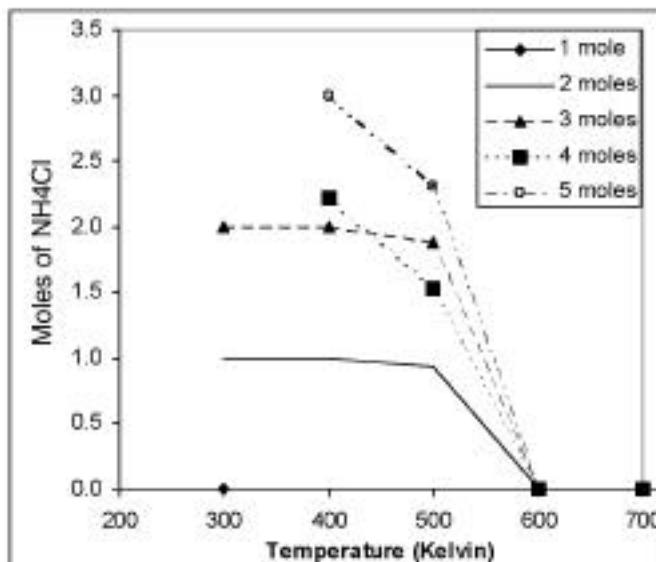


Figure 3: Relationship between the moles of NH_4Cl formed and the reaction temperature. Each line represents the amount of NH_3 that was used in the reaction.

Results

The deposition of boron nitride lines from BCl_3 and NH_3 was not successful. Instead, the only material to be deposited was some form of boron oxide and what is believed to be NH_4Cl . During the experiments, a white film that was believed to be NH_4Cl formed on the surface of the substrate. This hypothesis is plausible due to the lower temperature of the substrate and the surrounding reaction chamber. Experiments were conducted with the substrate globally heated to approximately 620 K with the same results.

Only a small amount of molybdenum was successfully deposited using MoCl_5 . Figure 4 is an SEM micrograph and EDS analysis of one of the attempts at depositing a line of molybdenum. This deposit was created at a deposition pressure of 5.0 psi, laser power of approximately 75 Watts, MoCl_5 flow rate of 6.22 sccm, sublimation chamber temperature of 150°C, and scan speed of 0.02 in/min. The partial pressure of the MoCl_5 was calculated to be 15 torr. The EDS analysis indicated that only a trace amount of molybdenum was evident on the substrate. The presence of oxygen was due to a bad seal on the sublimation chamber. The reagent powder had been contaminated with outside air.

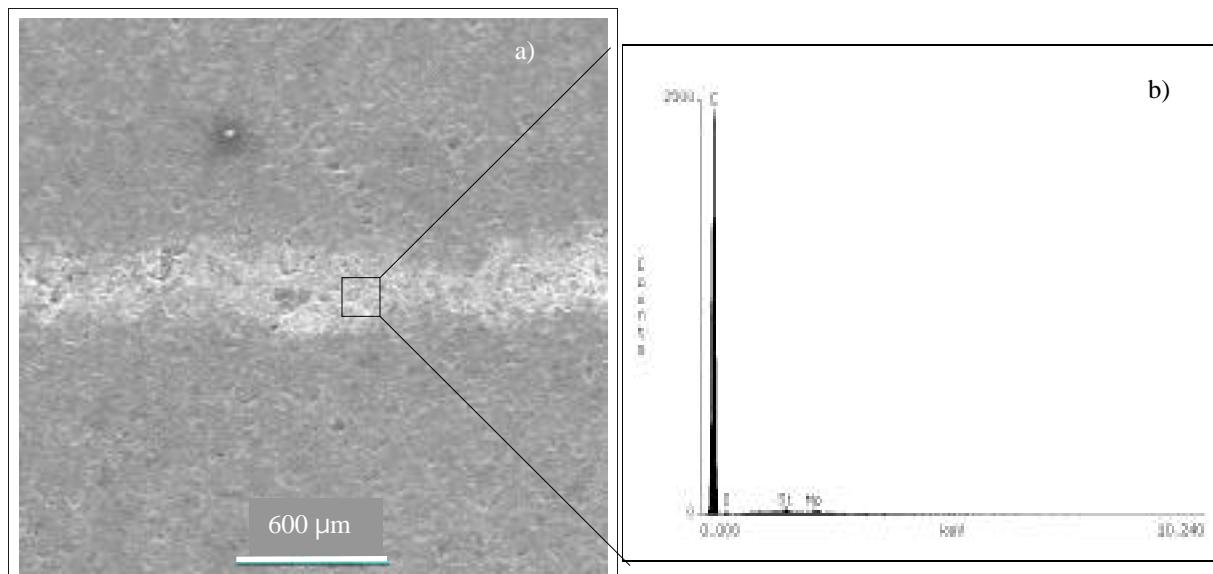


Figure 4: a) SEM micrograph and b) EDS analysis of the line produced by the attempt at depositing molybdenum.

Conclusions and Recommendations

Neither boron nitride nor molybdenum were successfully deposited in these experiments. However, LCVD-RP is still a possible manufacturing tool for depositing the structure necessary for the integrated-grid thermionic emitter. Because of the production of the by-product, NH_4Cl , depositing boron nitride from BCl_3 and NH_3 is not suited for this experimental system. Even though the substrate can be globally heated past the threshold temperature for the formation of NH_4Cl , the remainder of the reaction chamber is still at room temperature. The use of other reagents that do not require NH_3 , such as $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ (known as trichloroborazine or trichloroborazol),^{23,24} would eliminate the formation of NH_4Cl or any solid by-product.

Trace amounts of molybdenum were deposited using this experimental system. Due to the contamination of the reagent with air, the feasibility of using MoCl₅ as a reagent for depositing molybdenum is uncertain. In addition, no experimentation was attempted on depositing molybdenum onto previously deposited boron nitride. The morphology and characteristics of the deposit could be different on boron nitride than on graphite.

The manufacture of integrated-grid thermionic emitters via LCVD-RP is still a viable option. By using a different reagent for boron nitride, the formation of solid by-products could be eliminated. Further experimentation would be required to prove or disprove the use of MoCl₅ to deposit molybdenum.

Acknowledgements

The authors would like to thank Lisa Detter-Hoskin and Dr. Paul Kohl for the use of the SEM equipment and the glove box, respectively.

References

1. L. S. Nelson and N. L. Richardson, "Formation of Thin Rods of Pyrolytic Carbon by Heating with a Focused Carbon Dioxide Laser," *Material Research Bulletin*, 7, 971-976, 1972.
2. D. Bauerle, *Chemical Processing with Lasers*, Springer-Verlag: Berlin, 1986, 224, 71-93.
3. K. Mutoh, Y. Yamada, T. Iwabuchi, and T. Miyata, "Thickness Control of Multilayer Films in Laser-Induced Chemical Vapor Deposition," *Japanese Journal of Applied Physics*, 31, 1183-1184, 1992.
4. A. Silvestre, M Parames, and O. Conde, "Investigation of the Microstructure, Chemical Composition, and Lateral Growth Kinetics of TiN Films Deposited by Laser-Induced Chemical Vapour Deposition," *Thin Solid Films*, 241, 57-60, 1994.
5. J. Han, K. F. Jensen, Y. Senzaki, and W. Gladfelter, "Pyrolytic Laser Assisted Chemical Vapor Deposition of Al from Dimethylethylamine-alane: Characterization and a New Two-step Writing Process," *Applied Physics Letters*, 64 (4), 425-427, 1994.
6. Y. Morishige and S. Kishida, "Thick Gold-Film Deposition by High-Repetition Visible Pulsed-Laser Chemical Vapor Deposition," *Applied Physics A*, 59, 395-399, 1994.
7. H. Moilanen, S. Leppavouri, and A. Uusimaki, "Laser-Induced Chemical Vapor Deposition in Piezoresistive Pressure Sensor Fabrication," *Sensors and Actuators A*, 41-42, 150-155, 1994.
8. K.S. Boutros, J. C. Roberts, and S. M. Bedair, "Direct Writing of GaAs Optical Waveguides by Laser-Assisted Chemical Vapor Deposition," *Applied Physics Letters*, 68 (15), 2041-2042, 1996.
9. Han and K. F. Jensen, "Combined Experimental and Modeling Studies of Laser-Assisted Chemical Vapor Deposition of Copper from Copper(I)-Hexafluoroacetylacetone Trimethylvinylsilane," *Japanese Journal of Applied Physics*, 75 (4), 2240-2250, 1994.

10. G. Zong, "Solid Freeform Fabrication Using Gas-Phase Selective Area Laser Deposition," *Ph.D. Thesis*, University of Texas at Austin, 1991.
11. L. O'Conner, "Developing Bigger Micromachines," *Mechanical Engineering*, 82-83, February, 1996.
12. J. Maxwell and J. Pegna, "Experimental Developments Toward Multi-Material Micron Scale Rapid Prototyping," *ASME DE-Vol.82*, 1, 227-231, 1995.
13. J. Maxwell, M. Boman, K. Williams, K. Larsson, N. Jaikumar, and G. Saiprasanna, "High-Speed Laser Chemical Vapor Deposition of Amorphous Carbon Fibers, Stacked Conductive Coils, and Folded Helical Springs," *Part of the SPIE Conference on Micromachining and Microfabrication Process Technology V*, *SPIE* vol. 3874, Santa Clara, CA, 1999.
14. K. Williams, J. Maxwell, K. Larsson, and M. Boman, "Freeform Fabrication of Functional Microsolenoids, Electromagnets and Helical Springs Using High-Pressure Laser Chemical Vapor Deposition," *Proceedings of the 1999 12th IEEE International Conference on Micro Electro Mechanical Systems, MEMS*, 232-237, 1999.
15. Personal conversation with Dr. Wayne Ohlinger of Westinghouse-Bettis Laboratory. Dr. Ohlinger is an expert on the technology of thermionic emitters. August, 1998.
16. T. Matsuda, N. Uno, and H. Nakae, "Synthesis and Structure of Chemically Vapour-Deposited Boron Nitride," *Journal of Materials Science*, 21, 649-658, 1986.
17. W. Y. Lee, "Chemical Vapor Deposition of Dispersed Phase Ceramic Composites," *Ph.D. Thesis*, Georgia Institute of Technology, 1990.
18. T. Takahashi, H. Itoh, and A. Takeuchi, "Chemical Vapor Deposition of Hexagonal Boron Nitride Thick Film on Iron," *Journal of Crystal Growth*, 47, 245-250, 1979.
19. Y. Saeki and R. Matsuzaki, "Contributions to the Chemistry of Chlorides of Molybdenum. II. Thermodynamic Properties of Molybdenum Pentachloride," *Journal of the Electrochemical Society of Japan*, 33, 59-60, 1965.
20. C. E. Duty, D. L. Jean, and W. J. Lackey, "Design of a Laser CVD Rapid Prototyping System," *Ceramic Engineering and Science Proceedings*, 20 (4), 347-354, 1999.
21. D. L. Jean, C. E. Duty, B. T. Fuhrman, and W. J. Lackey, "Precision LCVD System Design with Real Time Process Control," *Proceedings Solid Freeform Fabrication Symposium*, 59-65, 1999.
22. JANAF Thermochemical Tables, 3rd Edition, Parts I and II; *Journal of Physical and Chemical reference Data*, 14, Supplement No. 1, 1985.
23. R. Stolle and G. Wahl, "Deposition of Boron Nitride Films from BB'B" - Trichloroborazine," *Journal De Physique IV*, 5 (5), C5-761 – C5-768, 1995.
24. R. Stolle and G. Wahl, "Direct Transfer of Kinetic Data from a Microbalance into a Tube Reactor for CVD BN on SiC Fabrics," *Chemical Vapor Deposition*, 6 (2), 83 – 92, 2000.