Vacuum Industries, Inc.
5 Middlesex Avenue
Somerville, Massachusetts 02145
Telephone: 617-666-5450
Telex: 681 7186

THE ROLE OF CVD IN CERAMICS PROCESSING

Paul J. Timmel, *Associate Product Manager*

TECHNICAL NOTE

Paper presented at 39th Pacific
Coast Regional Meeting of the
American Ceramic Society,
October 22-24, 1986
Seattle, Washington.

INTRODUCTION

Progress in the development of engineering ceramics has been closely related to advancements in processing technology. Chemical Vapor Deposition (CVD) techniques permit the fabrication of ceramic structures which have unique mechanical, electrical, thermal or optical properties. The use of CVD processes allows the formation of ceramic articles of extremely high purity for use in electronics processing, such as crucible materials. Application of high-temperature CVD techniques to ceramic processing is increasing because of better understanding of the chemistry of CVD processes, and is succeeding because an engineered approach to CVD systems design is being used.

CVD is rapidly growing in importance for the following reasons:

A. It is a versatile method for depositing a large variety of elements and compounds over a wide range of processing temperatures.
B. It is relatively easy to create materials over a wide range of accurately controllable compositions.
C. It can be used to form vitreous and crystalline layers which have a high degree of perfection and purity.
D. Layer structures and complex shapes can be formed by CVD that are difficult or impossible to form by other techniques.

The main applications of CVD processes are:

1. Preparation of oxidation-resistant and/or erosion-resistant materials, mostly for high temperature ($>1000^{\circ}C$) service, e.g., as nozzle material or coated electrodes.
2. Production of complex structural shapes by deposition on a sacrificial base material, which is removed after the CVD process (e.g., production of turbine wheels, tubes, precision parts).
3. Infiltration of porous ceramic materials to obtain dense composite structures with optimum oxidation and stress behavior.
4. Production of fibers, coated fibers, single crystals and epitaxial layers.

For each individual application the appropriate reactor for the special CVD process must be selected or modified.

DEFINITION OF CVD

A simplistic definition of CVD is the process of reacting gaseous constituents to form a film on a surface. It can be used to form thin films, thick films, or monolithic structures. The product that is obtained is dependent upon the precise control of the feedstock reactants and the process conditions within the reactor.

CVD has been utilized extensively in the semiconductor industry for buildup of layers upon silicon wafers. The process variations and reactor designs used in the semiconductor industry are too numerous to mention within the time frame of this talk. Also, these processes are routinely concluded at relatively low temperatures to avoid damage to the silicon substrates and organic masks. CVD, in the context of this presentation, shall be limited to CVD processes which occur at temperatures above 1000°C. These high-temperature CVD processes are used primarily to produce high-performance ceramic materials.

REACTIONS

In a typical CVD process, the gaseous reactants, usually involving halides, are injected into a heated volume. They react at specific temperature ranges to form a solid material plus gaseous by-products which may be highly acidic and/or toxic. These processes are typically inefficient, with a large percentage of the initial reactants being exhausted from the system without reacting.

A typical high-temperature CVD reaction occurs between Boron Trichloride (BCl_3) and Ammonia (NH_3) to form Boron Nitride (BN) plus Hydrogen Chloride (HCl). This reaction occurs in the temperature range between 1500°C and 1900°C.

$$BCl_3 + NH_3 \longrightarrow BN + HCl$$

A second typical high-temperature CVD reaction occurs between Dimethyldichlorosilane [$(CH_3)_2SiCl_2$] and Hydrogen (H_2) between 1300°C and 1500°C, producing Silicon Carbide (SiC), H_2 and HCl.

$$(CH_3)_2SiCl_2 + H_2 \longrightarrow SiC + H_2 + HCl$$

TYPICAL CERAMIC MATERIALS PRODUCED BY CVD

A broad range of ceramic materials can be produced by CVD techniques.

For example, CVD is one of the most effective means of preparing highly pure and dense silicon nitride (Si_3N_4) bodies. These bodies are obtained in amorphous or crystalline phases, depending on their deposition conditions. This reaction may proceed in the following manner:

$$SiCl_4 + NH_3 + H_2 \longrightarrow Si_3N_4 + HCl + H_2$$

A second example is the use of carbide, nitride and boride coatings applied by CVD. The coatings are finding greater use because they provide the wear resistance of the hard ceramic without the expense that would be incurred in producing complex, precise ceramic shapes.

Table 1 shows a variety of ceramic materials which can be formed by CVD and some applications of these CVD-ceramics.

TABLE 1

CVD CERAMICS

Materials	Applications
TiC, TiN, TiB_2, SiC	Wear-resistant coatings
TiN, TiC, SiC, PG (pyrolytic graphite)	Protect fibers
Al_2O_3	Form matrix of fiber-reinforced ceramic composites
SiC, Si_3N_4, B_4C, BN, TiB_2	
PBN, Si_3N_4, SiC	Bulk shapes
Ferrites	Magnetic bubble memory
Phosphosilicate glasses	Glass films for electronics

Much of CVD processing is still very much of an "art". A successful process is the happy marriage of the reactants, reactor design, hot zone design, operating conditions, etc. Alteration of any of these parameters typically results in a product which is different from that intended.

The following parameters must be considered for control of CVD reactions.

- starting precursor (feedstock)
- base material (possible reaction of surface)
- shape of work piece and position in furnace
- furnace dimensions and configuration
- flow of carrier gas
- gas composition and flow rate
- temperature and its distribution inside furnace
- pressure

From this review of the numerous variables which must be established and maintained, it becomes obvious that reliable equipment with controls capable of repeatable precision are paramount to success.

Let us turn our attention to system design considerations.

For large scale production, the system should perform with high throughput and economy in terms of power and feedstock chemicals. It should be simple, safe to operate and easy to maintain.

CVD SYSTEM DESIGN

Figure 1 illustrates the key components in any CVD system design: the chamber and hot zone, pumping system, temperature measurement and control, gas management and treatment of the effluent. These key subsystems will each be considered.

CHAMBER AND HOT ZONE

Chamber design for CVD usually considers ease of loading and maintenance of the system. The furnaces are typically vertically oriented, and the substrates to be coated can be loaded from the bottom or the top.

The size of the hot zone is determined by the dimensions of the part, the quantity of parts in the workload, and the length/width ratio which provides for the desired coating uniformity and reaction efficiency.

For intermediate and large capacities, a vertical, cylindrical hot zone in conjunction with an elevator hearth furnace which employs bottom loading is recommended. A typical VEH furnace is shown in Figure 2. There is some feeling shared among process people that the "chimney effect" obtained by gas injection at the bottom, with removal at the top, provides optimum distribution of flow. Other opinions hold that gas injection at the top with removal at the bottom counter-current to natural convection provides better coverage. In our opinion, a versatile furnace design which allows either mode is the best choice.

For high-temperature CVD, graphite resistance heating elements are typically used. The heating element assemblies are designed to provide temperature uniformity across the diameter of the hot zone. Hot zones may be designed to operate with a single zone of temperature control or to have multiple zones which are individually controlled to achieve temperature uniformity. Figure 3 illustrates a typical graphite heating element assembly installed in a furnace that provides an effective work space 24" diameter x 36" high. Note that the graphite tubes extend the entire length of the hot zone and provide uniform heat input.

Radiant heating with resistance elements is favored for controllability and uniformity from 1600°C to 2500°C. Multiple zone capability tends to be costly but necessary with high aspect ratio hot zones where length exceeds two-times the diameter or more. Silicon Controlled Rectifiers (SCR) and saturable reactor power supplies are used for adjusting furnace power input in connection with low voltage output power transformers. Hostile operating environments favor the use of totally enclosed, internally cooled power supplies. Heating by induction is used in cases where temperatures in excess of 2500°C are required and in extremely large furnaces.

The reaction of the corrosive feed gases and by-products with the heating elements and insulation must also be considered. The provision of a graphite muffle inside the hot zone can extend the life of the elements and, in particular, that of the graphite felt insulation by preventing contact with concentrated amounts of reaction gases. This effect can be enhanced by connecting the muffle to the pumping manifold, so that any outflow from the muffle is through the pumping system rather than into the furnace. The internals of a furnace showing the graphite muffle and pumping manifold are shown in Figure 4. A controlled pressure differential is used to maintain a net flow of inert, blanket gas from the furnace into the retort.

CVD is a tough environment for thermocouples. Optical pyrometry is preferred with most reactions conducted within the useful range of control. Temperature below 1200°C is usually unregulated in conjunction with current limiting to prevent overdriving the furnace. Systems requiring control at low temperatures may be equipped with retractable thermocouples which are withdrawn from the hot zone during the high-temperature portion of the cycle.

Insulation condition is monitored by a Type "K" thermocouple buried in the outer insulation layer. It also serves as an overtemperature protector.

Figure 5 shows a tandem pair of 24" diameter x 36" high effective hot zone CVD furnaces with elevator hearths, common power supply, control cabinets, and pumping systems (which are not shown). This arrangement allows one chamber to heat while the other chamber cools. Temperatures are sensed by optical pyrometers. Pressure is controlled by a feedback loop to a throttling valve. Flows of reactant and blanket gases are controlled by a separately packaged gas management system.

Figure 6 shows the bottom loading access lid which is equipped for installation of up to five gas injectors. An interchangeable access lid at the top provides unmatched versatility for load arrangement and establishing optimum reactant gas coverage in the hot zone. The full diameter top and bottom closures are used for periodic maintenance.

CVD reaction chambers can be made in a variety of sizes. Typical hot zone (work area) sizes and the corresponding chamber dimensions for six representative furnace sizes are presented in Table 2.

TABLE 2

Representative CVD Furnace work zone and chamber sizes.

WORK ZONE	CHAMBER
DIA x HEIGHT	DIA X HEIGHT
4" X 8"	20" X 22"
10" X 18"	24" X 36"
17" X 18"	36" X 48"
20" X 26"	42" X 60"
24" x 36"	50" X 82"
36" X 36"	66" X 96"

Let us turn our attention to the gas management system.

GAS MANAGEMENT SYSTEM

Strict attention must be paid to the storage and use of the CVD reactants. Most are gaseous at room temperature, some are liquid and many are extremely corrosive, toxic or both. Process gases are most frequently two reactive components with a third inert gas.

Delivery of the gases to the furnace hot zone is accomplished by using a graphite tube gas delivery system or by a specially designed water-cooled gas injector nozzle.

A gas delivery system does just that; it delivers gas through graphite tubes into the hot zone for reaction. Large flow rates may be required to prevent the feed gases from heating up too rapidly, thereby reacting in the gas delivery tube. A diluent gas such as Argon or Nitrogen is typically mixed with the feed gases to permit greater overall flow rates while maintaining the desired flow rates for the feed gases. The selected feed gases and diluent gas is first fed into a mixing chamber which is outside the furnace. The premixed gas is then delivered to the hot zone at a flow rate sufficient to prevent it from reacting until it exits from the gas delivery tube into the hot zone.

Cooled gas injector nozzles may be required to prevent premature reaction of the feed gases before they reach the hot zone. The injector nozzles may deliver two or three gases separately and simultaneously to the hot zone. Gas injector nozzles require water cooling for the parts within the furnace. Water cooling must be carried to the injector tip to allow it to withstand the hot, corrosive environment. Interruption of the cooling water supply or nozzle failure by corrosion can produce serious consequences involving costly repairs.

The remainder of the gas management system is based on a scale-up of technology widely used in the semiconductor industry.

Rotameters are most commonly used for manual flow control. Electronic mass flow controllers, developed for semi-conductor thin film CVD production, are becoming available in larger capacities and will supplant rotameters due to the advantage of precise, reproducible control by feedback circuitry. Balances are also used to monitor the weight loss of gas from the reactant containers. Plumbing in gas management and delivery systems must include purge lines for safety.

A throttle valve regulates the pressure in the reaction chamber. Pressure control is by feedback adjustment from an absolute pressure gauge. Flow rates for Low Pressure Chemical Vapor Deposition (LPCVD) processes in a 10 ft^3 reactor are typically 36 l/min at a furnace pressure of 500 microns. This is in combination with a pumping system having a large displacement on the order of 4000 cfm.

Temperature, time, pressure and process gas feed are programmed by multi-channel microprocessor instruments, providing for automatic operation and reproducibility of product cycle. Figure 7 shows a typical control panel containing the controls, recorder, push buttons and switches, gauges and alarms.

PUMPING AND HANDLING OF BY-PRODUCTS

Pumping systems for CVD reactors, shown schematically in Figure 8, typically consist of a mechanical blower/pump assembly and provide for large throughputs of gas flow from the reactor.

Operating pressures range from 500 microns to 50 torr with continuing efforts to push pressures higher for greater productivity.

Throttling features on roughing valves are employed to minimize dust clouds during initial pumpdown. Particulate filters are essential with careful attention to the manifold design to insure convenient access for removing accumulated dust resulting from imperfect CVD reactions.

A common reaction product is HCl. If prevented from hydrolyzing until it reaches a scrubber where it can be neutralized, costly corrosion can be minimized. Inert gas bleed at key points in the pumping system under certain conditions during the cycle requires experienced operators or sophisticated controls. An alternative to scrubbers is liquid ring pumps. Here, the corrosive reactants are dissolved in the liquid, and harmless gases are discharged from the system. In large scale operations, plant ventilation systems may also require scrubbers.

SYSTEM DESIGN

Selection of each of the key subsystems is critical in terms of its impact upon the success of the CVD system. A successful CVD system has each of these subsystems tailored to its system requirements. The CVD systems designer must be knowledgeable about the subsystem components, or have resources which can provide this technical expertise. A vacuum furnace manufacturer must be knowledgeable about various suppliers of the required subsystems and be able to make intelligent choices regarding proper sizing and compatibility of subsystem components. A combination of knowledge and experience contributes to the ultimate success and reliability of CVD systems.

Labor-saving automation and computerization are attractive options, and can be well worth the increased capital expenditure in reducing labor costs and improving the quality and reproducibility of the product.

SUMMARY

The continued penetration of CVD ceramic materials into the marketplace requires products with unique properties which can justify their high prices. Proper system design, reliability and successful scale-up are important aspects of increased market penetration.

* * *

CVD System Diagram

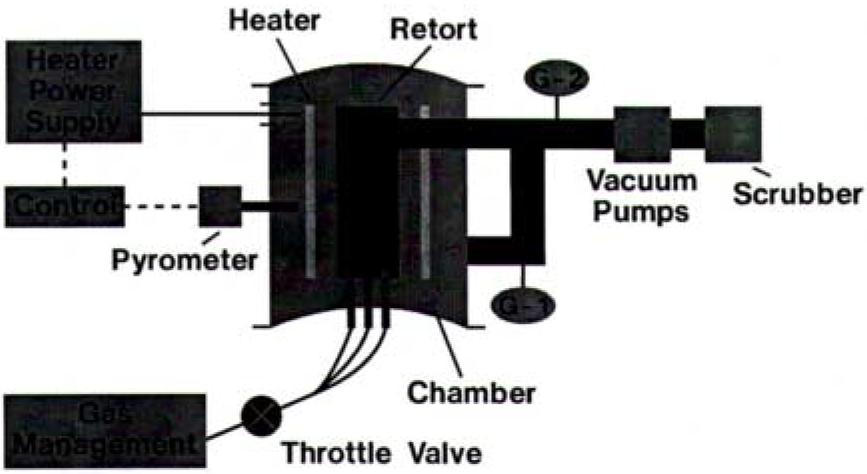

Fig. 1. High Temperature CVD System

Fig. 2. Typical Vertical Elevator Hearth CVD Furnace

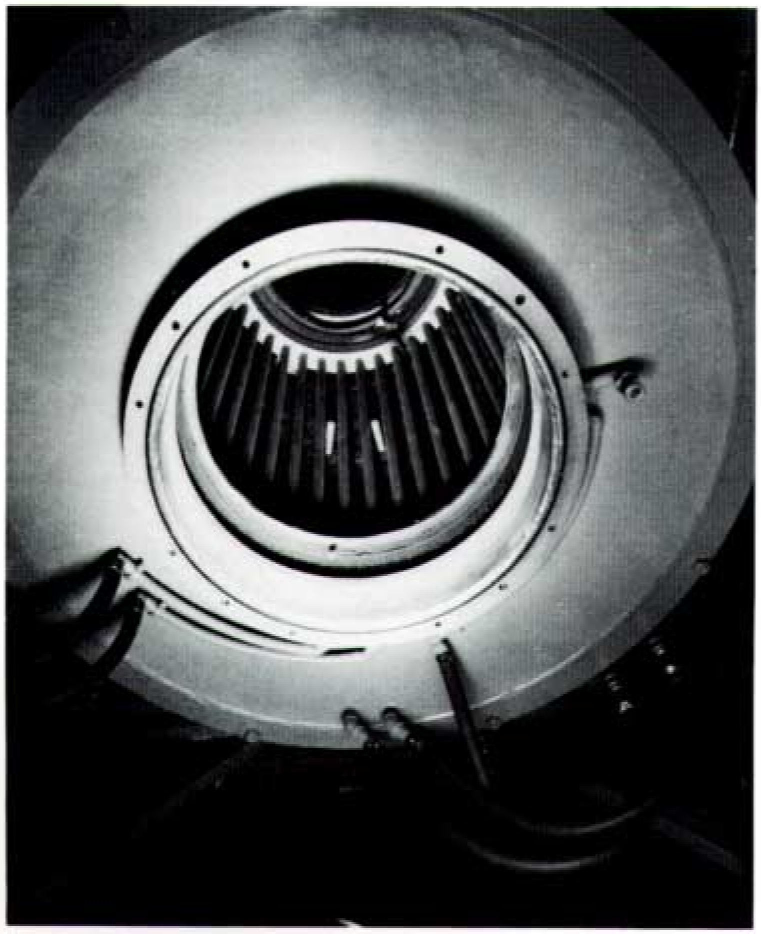

Fig. 3. Graphite Resistance Heating Element Assembly

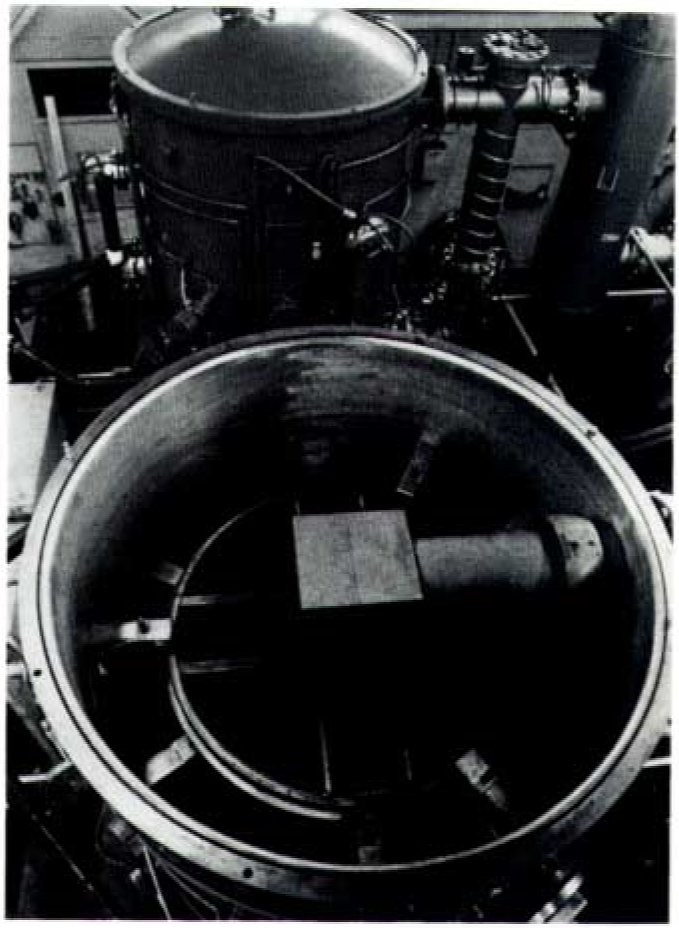

Fig. 4. Graphite Muffle in Resistance Heat Zone

Fig. 5. Tandem 24" Diameter by 36" High CVD Furnaces With Common Power Supply

Fig. 6. Access Lid for Bottom Loading on VEH CVD Furnace

Fig. 7. High Temperature CVD Furnace Control Console

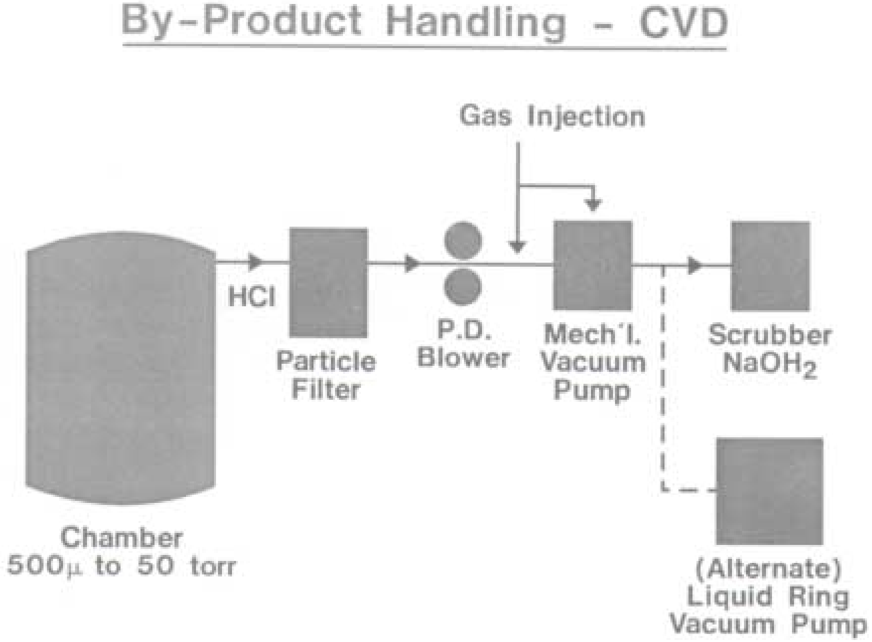

Fig. 8. Furnace Pumping System With By-Product Handling Provisions