



# Multilayer Ceramic/Metallic Coatings by Ion Beam-Assisted, Electron Beam Physical Vapor (EB-PVD) Deposition

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The covering or spreading of a layer over a surface is called a *coating*. This technological term is one of the oldest used in materials engineering and it still plays a significant role in our day-to-day life. Coatings play an important role in the advancement of technologies for applications in the microelectronics, optics, aerospace, and auto industries. For instance, multilayered ceramic/metallic coatings are used in the fabrication of components such as microelectronic chips and capacitors.

The performance of microelectronic chips depends on the coating process, thickness, and microstructure. Similarly, a high percentage (75%) of aircraft engine components are coated by metallic or ceramic coatings for the purpose of enhancing their performance and reliability. Thus, there is a continuous effort to engineer surface properties to enhance the life of components under severe environmental conditions where corrosion, high-temperature oxidation, and wear are concerns.

Before proceeding, three questions need to be answered.

1. What are coating processes?
2. What is the state-of-the-art of the ion beam-assisted, electron beam physical vapor deposition (EB-PVD) process?
3. What are the ideal applications for EB-PVD coatings ?

## Coating processes

Industrial coating processes (exclusive of painting and electroplating) can be broadly classified into three groups: physical vapor deposition (PVD), chemical vapor deposition (CVD), and metal spray. Each process can again be subclassified based on the source of energy used for the deposition of coatings as shown in Table 1. Each of these processes have advantages and disadvantages. For example, chemical and physical conditions during the deposition reaction can strongly affect the composition, residual stresses, and microstructure (i.e., amorphous,

Table 1: *Coating Deposition Techniques.*

Spray Deposition processes
Thermal spray
High-Velocity Oxy-fuel (HVOF)
Detonation gun (D gun)
Chemical Vapor Deposition processes (CVD)
Low-pressure CVD
Plasma-enhanced CVD
Photochemical and laser CVD
Physical Vapor Deposition processes (PVD)
Thermal evaporation
Electron beam evaporation
Sputtering
Balanced and unbalanced magnetron sputtering
– Direct current diode sputtering
– Radio frequency sputtering
– Triode-assisted PVD
Ion Implantation and Ion Plating

polycrystalline, epitaxial, texture) of the product and must be understood to control the process. Thus, the coating thickness, properties (including microstructural, physical, and mechanical), and applications will determine the coating process to be used.

In the *spray* processes, pre-alloyed powder is injected along with the carrier gas through the high-energy source. Unfortunately, the spray process often produces an inhomogeneous microstructure containing defects including unmelted particles, oxide layers, and voids. The deposited coatings are thick, usually several hundred microns or more (>100 μm). A significant advantage of this process is the high deposition rate (100–1000 μm/minute) and the fact that various metallic and oxides coatings can be applied. Disadvantages of the spray processes are the inability to obtain homogenous, high-quality, and dense coatings (especially carbides and nitrides).

Some of the difficulties associated with the spray coating were overcome by *chemical vapor deposition* (CVD) processes. The term CVD is defined as a process whereby constituents of a gas or vapor react chemically in a vacuum chamber to form a solid product in the form of a thin film at the substrate surface. The CVD coating process takes place between temperatures of 1,000 to 2,000°F. Various metallic and ceramic (oxides, carbides, nitrides) coatings can be deposited by this process at a rate of 5–10 μm/hour. The residual stresses in a CVD coating are

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generally tensile. The disadvantages of CVD processes are: they produce chemical wastes; it is difficult to accommodate large components; and the process requires high temperatures.

These shortcomings of the CVD process are addressed by *physical vapor deposition* (PVD). The term PVD denotes those vacuum deposition processes where the coating material is evaporated by various mechanisms (resistant heating, high-energy ionized gas bombardment, or electron gun) under vacuum, and the vapor phase is transported to the substrate, forming a coating. PVD is a line-of-sight process in which atoms travel from a metallic source to the substrate on a straight path. The residual stresses in the PVD coating are generally compressive. Compressive stresses retard the formation and propagation of cracks in the coating. This is particularly advantageous for applications such as thermal barrier coatings (TBC). The PVD coating process takes place between 200 to 1,000°F. Sputtering is one of the most versatile PVD processes available for thin film preparation. Various metallic and ceramic (carbides and nitrides) coatings can be applied by this process at a rate of a few  $\mu\text{m}$  or less per hour. Unlike the CVD process, PVD processes are clean and pollution free. The main disadvantages of PVD processes (with exception of EB-PVD) are the low deposition rates and the difficulty to apply oxide coatings efficiently.

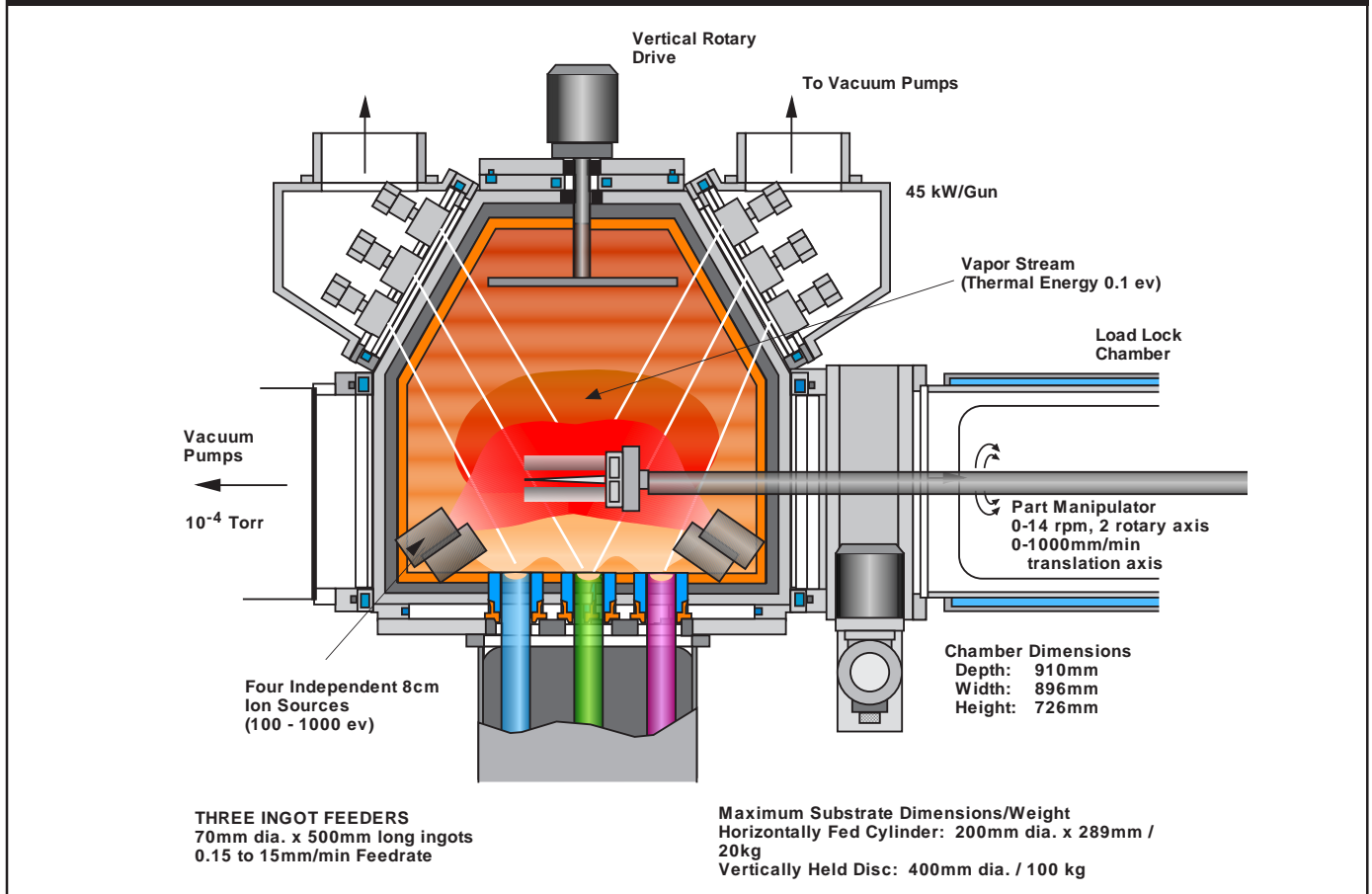
Ion implantation is another process of surface modification of materials by imbedding in it appropriate atoms in the form of a beam of ionized particles. High-energy ions are produced in an accelerator and directed on the surface of the substrate. A high-energy ion implanter (1–10 MeV) is required for deep penetration ( $\sim 5 \mu\text{m}$ ). Ionized particles enter into the substrate with kinetic energies four to five orders of magnitude greater than the binding energy of the solid. The principal application of ion implantation has been in the electronic industries. The disadvantages of the ion implantation process are the limited depth of penetration in the substrate ( $< 5 \mu\text{m}$ ) and high equipment cost.

Ion plating is the derivative of ion implantation in which the substrate is made into a cathode and the material to be coated is thermally evaporated (or in some cases, sputtered). The ion plating process is very similar to the PVD process. By the proper selection of materials and gas, carbides, nitrides, and oxides can be reactively deposited. Potential applications for ion plating are in the tool industries and selective aircraft components. The disadvantages of the ion plating process is the low deposition rate (0.03 to 0.3 nm/sec) and the high equipment cost.

The *electron beam physical vapor deposition* (EB-PVD) process is considered to be a relatively new technology and it

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Figure 1: EB-PVD schematic.



has overcome some of the difficulties or problems associated with the CVD, PVD, or metal spray processes. In the EB-PVD process, focused high-energy electron beams generated from electron guns are directed to melt and evaporate ingots as well as preheat the substrate inside the vacuum chamber as shown in Figure 1.

The EB-PVD process offers many desirable characteristics such as relatively high deposition rates (100–150  $\mu\text{m}/\text{minute}$  with an evaporation rate of 10–15  $\text{Kg}/\text{hour}$ ), dense coatings, precise composition control, columnar and polycrystalline microstructure, low contamination, and high thermal efficiency. Various metallic and ceramic coatings (oxides, carbides, nitrides) can be deposited at relatively low temperatures. Even elements with low vapor pressure such as molybdenum, tungsten, and carbon are readily evaporated by this process. In addition, it is capable of producing multilayered laminated metallic and ceramic coatings on large components, by changing the EB-PVD processing conditions such as ingot composition, part manipulation, and EB energy. The main disadvantage of the EB-PVD process is the high capital equipment cost.

Attachment of an ion-assisted beam source to the EB-PVD offers additional benefits such as dense coatings with improved adhesion. In addition, textured coatings can be obtained that are desirable in many applications such as optics and microelectronics as well as high-wear applications such as cutting tools. The state of the internal stresses developed in the coating can be changed from tensile to compressive stress by the forcible injection of high-energy-beam atoms (i.e., ion implantation). Thus, the ability to control stress levels in the multilayered coatings is an additional feature of the ion beam-assisted processing. Also, a high-energy ion beam (as a source of energy) is quite often used to clean the surface of the specimen inside the vacuum chamber prior to coating. This cleaning enhances the mechanical bonding strength between the coating and the substrate.

Many coating materials are used both in the microelectronics and heavy manufacturing industries. For example, oxides of aluminum, yttrium, zirconium (i.e.,  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$ , respectively) are used in microelectronic industries as an insulator, buffer layer, or diffusion barrier coatings. The thickness of coatings for such applications is  $<10 \mu\text{m}$ .

Oxide coatings are also used in the aerospace and auto industries for enhancing the performance of components under severe, high-temperature environmental conditions where corrosion, oxidation, and high wear are of interest. The coating thickness for such applications is typically  $>10 \mu\text{m}$ . Such coatings are often called *thermal barrier coatings* (TBC).

Multilayered metallic or ceramic coatings are often applied on the components to achieve the desired properties. The properties and performance of the coating also depends upon the coating thickness. It has been well established that multilayered coatings with a thickness of  $<1 \mu\text{m}$  offer superior structural

and physical properties due to a refined microstructure in the coating and good interfacial bonding with the substrate.

In summary, the choice of a deposition technique is determined by the application for the coating, the desired coating properties, cost or production rate available from the process, temperature limitation of the substrate, uniformity or consistency of the process, and its compatibility with subsequent processing steps. Chemical and physical conditions during the deposition reaction can strongly affect the microstructure of the coating (i.e., single crystalline, polycrystalline, amorphous, epitaxial).

### Applications

Versatility of the EB-PVD process appears unlimited and new varieties of coatings and materials continue to be developed. Successful applications of the EB-PVD and ion beam-assisted EB-PVD processes are given below:

#### Optical coatings

Ion beam-assisted EB-PVD processes can be used to apply thin oxide films of  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{HfO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZnO}$  for optics, high-performance solar cells, and sensors. Performance of these films depends on the quality of the thin films including uniformity, density, and texture. Currently, conductive transparent films of indium-tin-oxide are being applied by the ion beam-assisted EB-PVD process.

#### Microelectronic coatings

High-quality, defect-free epitaxial or textured thin films are desired in the microelectronic industries. Varieties of ceramic and metallic multilayered coatings are used as a buffer layer in the microelectronic industries to achieve desired properties such as diffusion barrier coatings for epitaxial growth textured thin films. To grow epitaxially superconducting thin films of YBCO (yttrium barium copper oxide) on stainless steel plates, various multilayer oxide films ( $\text{Al}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{CeO}_2$ ) are deposited by various techniques including sputtering, ion beam-assisted sputtering, and laser ablation. Such intermediate layers are essential to obtain good quality, superconducting thin films. These coating thickness varies from  $100 \text{ \AA}$  to  $1 \mu\text{m}$ . These same coatings can also be obtained by the ion beam-assisted EB-PVD processes at a relatively low cost.

#### Coatings for heavy-duty turbine, auto, and aerospace industries

The EB-PVD process has been used successfully in applying oxidation and wear-resistant multilayered metallic/ceramic coatings at a high deposition rate on large components such as turbine blades. The thickness of these coatings varies from 0.1 mm to 5 mm depending on the application. Thick metallic/ceramic coatings (including TBC) were previously applied by the spray processes. The life of the plasma-sprayed TBC-coated turbine component was limited due to the inhomogeneous microstructure, unmelted particles, voids, and poor bonding

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with the substrate. When the same coating was applied by the EB-PVD process, the life of component was reported to increase by a factor of two (2×) due to the dense columnar microstructure with an improved mechanical bonding with the substrate.

### Coatings for tool and die industries

A remarkable improvement in tool life was observed (at least 100%–400%) after applying hard wear-resistant coatings (such as TiC, TiN, TiAlN, TiZrN). The performance of these wear-resistant coatings depends on the composition and coating processes including PVD and CVD. Since CVD is a high-temperature process (1,300–1,800°F), many temperature-sensitive substrates cannot be coated by this method. Low-temperature PVD processes have met the demands of the tooling market. Coating performance can be further enhanced by high-energy ion bombardment or applying the coating with an ion beam-assisted PVD process. Similar results can be obtained with ion beam-assisted EB-PVD processes.

### Corrosion-resistant coatings

A unique characteristic of EB-PVD is that it can be used to tailor-make dense coatings for specific applications. This ability to tailor surface properties is especially useful when corrosion is a concern. With the EB-PVD process, high-cost, corrosion-resistant materials can be applied economically on the surface where they are most needed. This technology offers a cost-effective alternative to simply manufacturing the entire component from a more costly material. Unlike thermal spray coatings, these deposits are fully dense and sealers are not required in order to attain corrosion resistance. Applications for these coatings range from brass lighting fixtures to Al-based metal matrix composites for advanced aerospace structures. In addition to coating composition and structure, deposit morphology and residual stress characteristics of the EB-PVD process significantly enhances the corrosion-resistant properties.

### EB-PVD research facilities and capabilities at Penn State

1. Ion Beam-Assisted EB-PVD: general coater  
*One 10-kW gun, cold cathode ionization source, four hearths, cryopump, chamber size 66 cm × 60 cm.*
2. EB-PVD: general coater  
*Two 15-Kw guns, two hearths, cryopump, chamber size 66 cm × 60 cm.*
3. EB-PVD: general coater  
*Six 45-kW guns, three continuous feed ingots, chamber size 900 cm × 900 cm × 900 cm.*
4. EB-PVD: fiber coater.

For intelligent processing, in-situ coating characterization facilities such as the X-ray diffractometer (for monitoring phase composition, grain size, and orientation), atomic absorption spectrometer (for measuring the elemental concentration in the vapor cloud), crystal microbalance (for thickness measurement), and dual-wave pyrometer (temperature monitor) will be incorporated with the EB-PVD units. This financial support was given by U.S. Air Force Scientific Office of Research (AFSOR) in Washington, D.C. This will be a state-of-the-art EB-PVD coating research facility.

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