



Electron Beam Physical Vapor Deposition Technology: Present and Future Applications

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Electron beam-physical vapor deposition (EB-PVD) is a derivative of the electron beam melting technique. [Records reveal the first U.S. patent was issued to M. Von Pirani in EB melting and refining of materials in March 1907.] Perhaps the most consequential growth phase in EB technology began in the early '80s and is still in progress. This significant progress was driven by three factors: (1) much improved vacuum generation technology, (2) significant advances in computers, and (3) availability of high-quality EB guns. Since then, EB gun technology is constantly gaining reputation and confidence in industrial applications including cutting, welding, melting and refining, and coatings.

The covering or spreading of a layer over the component surface is called coating. Coating is one of the oldest technological terms used in materials engineering. The role of coatings is significant in the advancement of technologies for applications in the microelectronics, optics, auto and aerospace industries. A high percentage (75%) of aircraft engine components is coated by metallic or ceramic coatings for the purpose of enhancing 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. Similarly, multilayered ceramic and metallic coatings are used in the fabrication of components such as micro-electronic chips and capacitors.

Before proceeding, three questions need to be answered:

1. What are coating processes?
2. What is the uniqueness of the EB-PVD process?
3. What are 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 has 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, polycrystalline, epitaxial, and texture) of the product and must be understood to control the process. Thus, coating thickness, desired properties (including micro-

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

structure, physical, and mechanical properties), and the application will determine the coating process to be used.

In the spray process, pre-alloyed powder is injected along with a carrier gas through a high-energy source. The coating candidate material is transferred in the form of molten or semi-molten droplets and directly deposited onto the components. The principle of the process is to feed powder into the plasma where the particles are rapidly heated to their melting point and accelerated to speeds the order of 300 m/sec. After a few milliseconds, the molten powder particles strike and flatten on the object surface and rapidly solidify. The adhesion of the particles to the substrate is mainly a mechanical bond. The rate of coating deposition and the quality of the coatings (density) depends upon the spray process selected (i.e., D-gun, HVOF, plasma-transferred arc processes, etc.), the processing parameters, and the coating and substrate materials used. A significant advantage of this process is the high deposition rate (100-1,000 m m/minute) and the fact that various metallic and oxide coatings can be applied. Disadvantages of the spray processes are the inability to obtain homogenous, high-quality, and dense coatings.

Some of the difficulties of the spray process were overcome by the chemical vapor deposition (CVD) process. The term CVD is defined as a process whereby a reactant gas mixture is passed in a high-temperature reactor 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 800 and 1200° C. Various metallic and ceramic (oxides, carbides, and nitrides) coatings have been deposited at a rate of 5-10 pm/hour. The disadvantages of the CVD process are :they often require high-deposition temperatures (>1000° C); they produce chemical waste (such as hydro-

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chloric acid, etc.) that is environmentally unacceptable; deposition rates are usually slow (>100 A/minute) for high-quality coatings; and it is difficult to accommodate large components.

The shortcomings of the CVD process are addressed by the physical vapor deposition (PVD) process. 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. The PVD coating process takes place between temperatures of 100°-600° C. 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 typically at a rate of a few m 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 EEPVD) are the low deposition rates and the difficulty in applying oxide coatings efficiently.

In spite of significant advancements in the various PVD processes (such as cathodic-arc and unbalanced DC and RF unbalanced-magnetron sputtering), there are still drawbacks in coating quality. For example, the cathodic-arc PVD process produces liquid droplets or macro-particles of metals, 1 µm to 15 µm in size, during the evaporation of the target material. These molten particles can be trapped into the growing film on the substrate, resulting in nonhomogeneity in the microstructure and reducing its physical properties. In the unbalanced (DC) magnetron sputtering process, multiple cathodes produce a plasma of inert-gas ions, which then eject atoms out of the source material. Metallic atoms from the source material are deposited on the surface of the substrate, where they combine with the reactive gas to form the coating (e.g., TiN, NbN, etc.). The unbalanced (DC) magnetron sputtering is limited to reactive gases (e.g., nitrogen, methane, etc.). The main disadvantages of sputtering PVD processes (with the exception of EB-PVD) are the low deposition rates (1-10 µm per hour) and the difficulty in applying oxide coatings efficiently. Shortcomings of sputtering were overcome by the EB-PVD process.

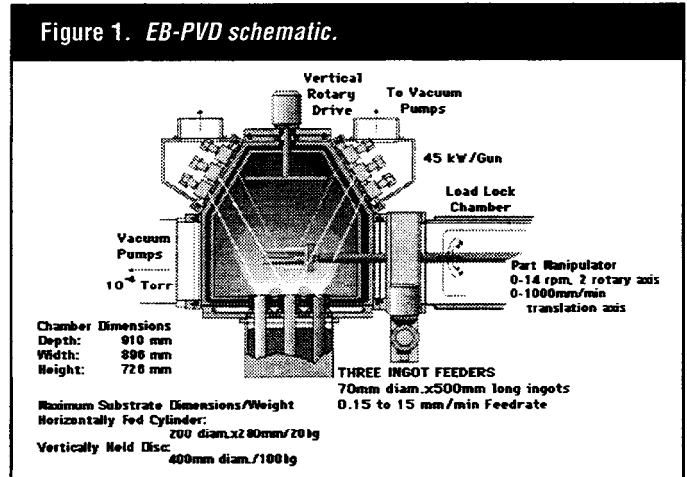
Ion implantation is not a coating, but is another process of surface modification of materials by imbedding in it appropriate atoms by means of a beam of ionized particles. High-energy ions are produced in an accelerator and directed on the surface of the substrate. A high-energy ion implanter (1-10 MeV) is required for deep penetration (~5 µm). Ionized particles enter into the substrate with kinetic energies four to five orders of magnitude greater than the binding energy of the solid by a collision mechanism. The principal application of ion implantation has been in the electronic industries. The disadvantage of the ion implantation process is the limited depth of penetration in the substrate (< 5µm).

Ion plating is the derivative of ion implantation in which the substrate is made 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 deposited. Potential applications of ion plating are in tool industries and certain aircraft components. The disadvantage of the ion plating process is the low deposition rate (0.03 to .3 rim/sec).

The EB-PVD Process

The electron beam-physical vapor deposition process has overcome some of the difficulties associated with the CVD, PVD, and 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 to preheat the substrate inside the vacuum chamber. (See Figure 1).



ARL Penn State's industrial pilot Sciaky EB-PVD unit has six electron beam guns, four of which are used to evaporate the coating materials and two of which are used to preheat the substrate to facilitate coating adhesion. Each gun has a 45-kW capacity. The chamber will accommodate up to three ingots ranging in size from 7-15 cm in diameter and 70 cm long. The overall dimensions of the production unit is about 1 cubic meter. [The maximum diameter of the substrate (with vertical rotation) that can be accommodated is about 400 mm; and can be rotated at a speed of 5.5 to 110 rpm with a maximum load of about 100 Kg.] The unit also has a horizontal sample holder with a three-axis part manipulator: two rotary axes of C-14 rpm and a 0-1,000 µm/min translation axis. It can carry samples weighing up to 20 kg. Physical vapor deposition is primarily a line-of-sight process; therefore uniform coatings of complex parts (such as turbine blades) can be accomplished by continuously rotating the part during the coating process.

Advantages of the EB-PVD Process

The EB-PVD process offers extensive possibilities for controlling variations in the structure and composition of condensed materials. For example, the coating compositions can be varied continuously, as in so-called Functional Gradient Coatings (FGC). Also, coatings comprised of alternating layers of different compositions can be made. These multilayered coatings can be applied on top of the FGC. The EB-PVD process offers many desirable characteristics such as relatively high deposition rates (up to 150 µm/minute with an evaporation rate of ~10 - 105 Kg/hour), dense coatings, composition control, columnar and polycrystalline microstructure, low contamination, and high thermal efficiency. Coatings produced by the EB-PVD process usually have a good surface finish and a uniform microstructure. The microstructure and composition of the coating can be easily altered by manipulating the process parameters and ingot compositions. Thus, multilayered ceramic/metallic coatings can be readily formed and various metallic and ceramic coatings (oxides, carbides, and 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.

The attachment of an ion beam-assisted source to the EB-PVD system offers additional benefits such as forming dense coatings with

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improved microstructure, interfaces, and adhesion. In addition, textured coatings, that are desirable in many applications, can be obtained. The state of the internal stresses can be changed (i.e., from tensile to compressive) by the forcible injection of high-energy ion beams (100-1,000 eV). 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. The 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., Al_2O_3 , Y_2O_3 , ZrO_2 , respectively) are used in microelectronic industries as an insulator, buffer layer, or diffusion barrier coating. The thickness of coatings for such applications is < 10 μm . On the other hand, in the aerospace and auto industries, oxide coatings are used for enhancing the performance of components under severe environmental conditions such as corrosion, oxidation, and wear. The coating thickness for such applications is typically > 10 μm . Such coatings are often called thermal barrier coatings (TBC).

Multilayered metallic or ceramic coatings are often applied on the components to achieve desired properties. Properties and performance of the coating also depends upon the coating thickness. It has been well established that multilayered coatings with thickness < 1 μm offer superior structural and physical properties due to refined microstructure in the coating and good interfacial bonding with the substrate.

In summary, the choice of 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 resultant microstructure of the coating (i.e., single-crystalline, polycrystalline, amorphous, epitaxial).

Applications of the EB-PVD Process

The versatility of the EB-PVD process is very wide and new varieties of coatings and materials continue to be developed. Some successful applications of the EB-PVD and ion beam-assisted EB-PVD processes are given below.

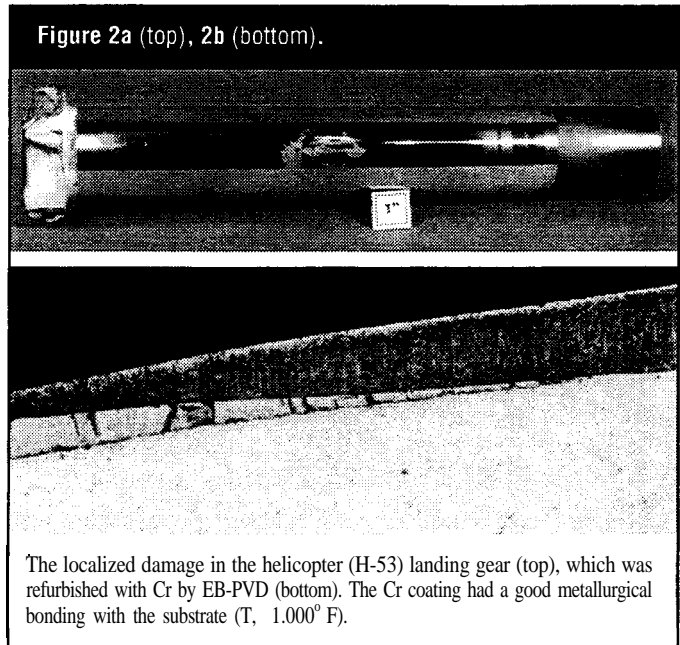
ALTERNATIVE TO HARD CHROME ELECTROPLATING CORROSION-RESISTANT COATINGS.

Chromium (Cr) electroplating is well known to be an environmentally hazardous process. The Cr plating process is normally used in areas where wear, corrosion, and oxidation ($< 600^\circ C$) are factors in equipment performance. An environmentally friendly process which provides the same or improved wear, corrosion, and oxidation protection is required. To achieve this goal, two challenges must be met: (1) identify/develop potential candidate materials for the replacement of Cr and (2) develop/identify a process for applying the candidate coating materials.

A unique characteristic of EB-PVD is that it meets the above mentioned challenges and also can be used to tailor coatings for specific applications. With the EB-PVD process, corrosion-resistant materials can be applied economically on the surface where they are most needed. Applications for these coatings range from brass lighting fixtures to landing gear and other components of aircraft and helicopters.

Figure 2a is a photograph of a helicopter landing gear showing localized surface damage that needs to be repaired. The current repair

process is the chemical stripping of the chromium coating followed by replating, baking, and machining of the entire component. Localized refurbishment of the landing gear (Figure 2b) was successfully demonstrated by applying Cr in the EB-PVD chamber. Unlike thermal spray coating, these deposits had a dense microstructure with good metallurgical bonding with the base metal. In addition, microcrack sealers are not required. The cost saving is expected to be more than 20-30% with improved component life and performance. Efforts are underway to identify alternative chromium replacement materials (deposited below $500^\circ F$) which will have superior physical and mechanical properties under severe environmental conditions.



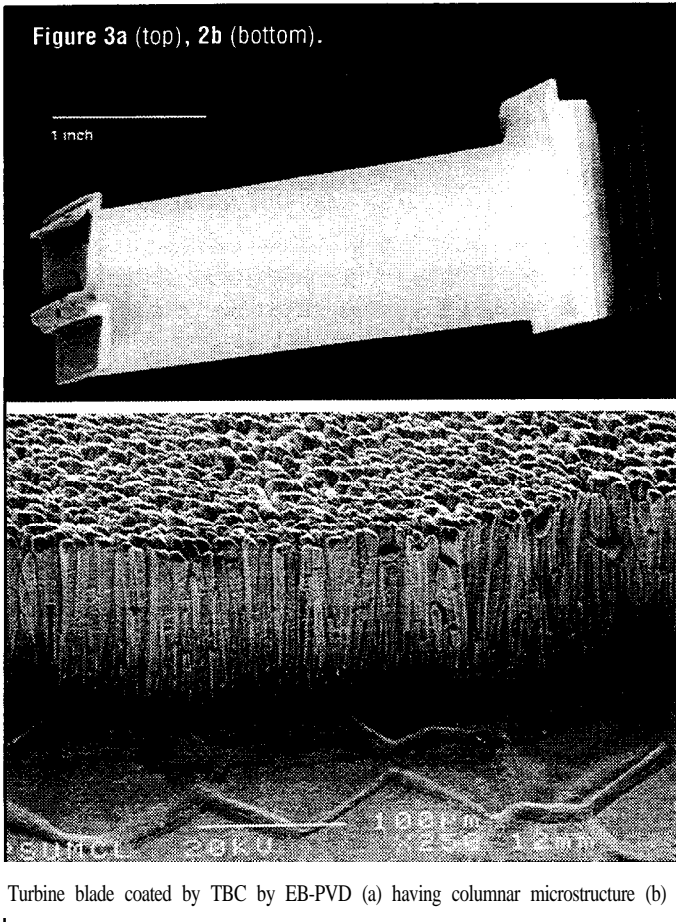
COATINGS FOR THE TURBINE INDUSTRY

The EB-PVD process has been used successfully in applying oxidation and wear-resistant metallic and ceramic coatings at high deposition rates on large components such as turbine blades. The thickness of these coatings varies from 0.1 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 with the substrate. When the same coating is applied by the EB-PVD process as is being done commercially, the life of the component is reported to increase by a factor of two due to the porosity controlled columnar microstructure, smooth surface finish, and improved metallurgical bonding with the substrate (Figure 3). Future thrusts are in producing a compositional gradient and oxidation-resistant bond coat as an intermediate layer followed by low-conductivity, porosity-controlled TBCs. Additional future efforts include developing advanced spar-shell structures for turbine blades. Overall it is anticipated that the DoD goal of doubling thrust-to-weight ratios for aircraft engines can be achieved.

COATINGS FOR TOOL AND DIE INDUSTRIES

A remarkable improvement in tool life was observed (at least 400%- 600%) after applying hard wear-resistant coatings (such as TIC,

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Turbine blade coated by TBC by EB-PVD (a) having columnar microstructure (b)

TiN, TiAlN, and TiZrN). Performance of these wear-resistant coatings depends both on composition and the coating process. Nitride coatings are commercially applied by the PVD process (Table 1) whereas carbide coatings (such as TiC, HfC, ZrC) are applied by CVD. Since CVD is a high-temperature process (800-1200°C), many temperature-sensitive substrates cannot be coated by this method.

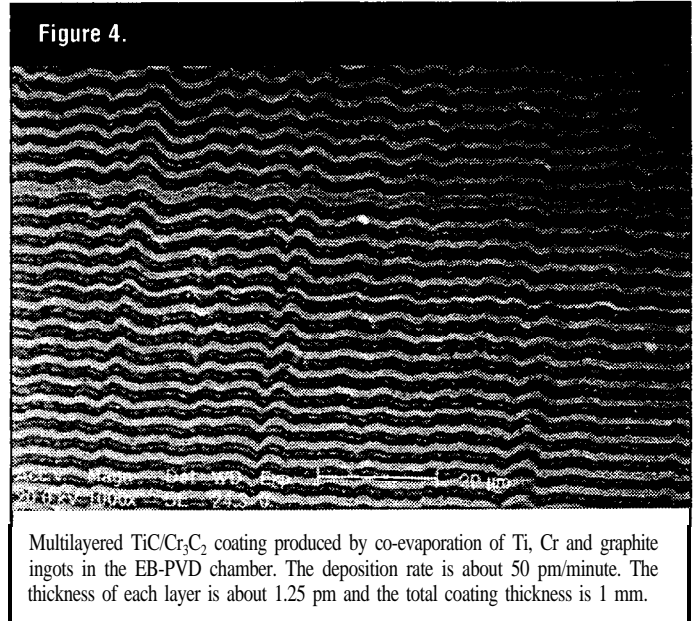
EB-PVD has overcome some of the problems associated with CVD, including environmental issues, waste of hazardous chemical gases, undesirable high-temperature reactions, and low deposition rate. Hard coatings such as TiC, HfC, ZrC, TiN, and TiB₂ have been economically produced by ion beam-assisted EB-PVD at relatively low temperatures. Multilayered coatings composed of TiC/Cr₃C₂ have been successfully produced by the co-evaporation of the Ti, Cr, and graphite ingots in the EB-PVD chamber (Figure 4). The future thrust is in developing superhard multilayered coatings composed of Al₂O₃/TiC and TiB₂/TiC/Cr₃C₂ by the ion beam-assisted EB-PVD.

OPTICAL COATINGS

The ion beam-assisted EB-PVD process has been successfully used to apply thin films of various materials including Ag, Cu, ZrO₂, TiO₂, Al₂O₃, and SiO₂, 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.

MICROELECTRONIC COATINGS

High-quality, defect-free epitaxial or textured thin films are desired in the microelectronic industry. Varieties of ceramic and metallic multilay-



ered coatings are used as a buffer layer to achieve properties such as diffusion barrier coatings for epitaxial growth textured thin films. To grow epitaxially superconducting thin films of yttrium barium copper oxide (YBCO) on stainless steel plates, various multilayered oxide films (Al₂O₃ or Y₂O₃, ZrO₂, and CeO₂) 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. The thickness of these coatings varies from 100 Å to 1 μm. These same coatings can also be obtained by the ion beam-assisted EB-PVD process at a relatively low cost.

EB-PVD Research Facilities and Capabilities at Penn State

1. EB-PVD industrial coater
Six 45-kW guns, three continuous feed ingots, chamber size: 1 cubic meter with load lock chamber and Kauffman type ion source.
2. Ion Beam-Assisted EB-PVD general coater
One 10-kW gun, four hearths, cold cathode ionization source, cryo-pump, chamber size: 66 cm x 60 cm.
3. EB-PVD
Two 15-Kw guns, two hearths, cryo-pump, chamber size: 66 cm x 60 cm.



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