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Session D
Physical Vapor Deposition

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AN INTRODUCTION TO PHYSICAL VAPOR DEPOSITION (PVD) PROCESSES©

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For AESF SUR/FIN '92

ABSTRACT

Physical Vapor Deposition (PVD) processes are atomistic deposition processes in which material vaporized from a source is transported in the form of a vapor through a vacuum or low pressure gas environment to the substrate where it condenses and film growth takes place. PVD processes may be used to deposit films of compound materials by the reaction of depositing material with the ambient gas environment or with a co-deposited material. The three basic PVD techniques are: vacuum evaporation, which uses thermal evaporation as a source of depositing atoms, sputter deposition, which used physical sputtering as the source of depositing atoms, and ion plating which uses concurrent ion bombardment during deposition to modify the film growth.

INTRODUCTION

Physical Vapor Deposition (PVD) processes are atomistic deposition processes in which material vaporized from a source is transported in the form of a vapor through a vacuum or low pressure gas environment to the substrate where it condenses. PVD processes may be used to deposit films of compound materials by the reaction of depositing material with the ambient gas environment or with a co-deposited material. The three basic PVD techniques are: vacuum evaporation, which uses thermal evaporation as a source of depositing atoms, sputter deposition, which uses physical sputtering as the source of depositing atoms, and ion plating which uses concurrent ion bombardment during deposition to modify the film growth and properties. A fourth technique which can be considered to be a type of ion plating is Ion Beam Assisted Deposition (IBAD) which uses concurrent bombardment from an "ion gun" in vacuum to modify the film growth and properties. The various PVD techniques are shown in Figure 1. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers* to thousands of nanometers; however they can be used to form multilayer coatings, very thick deposits and freestanding structures.

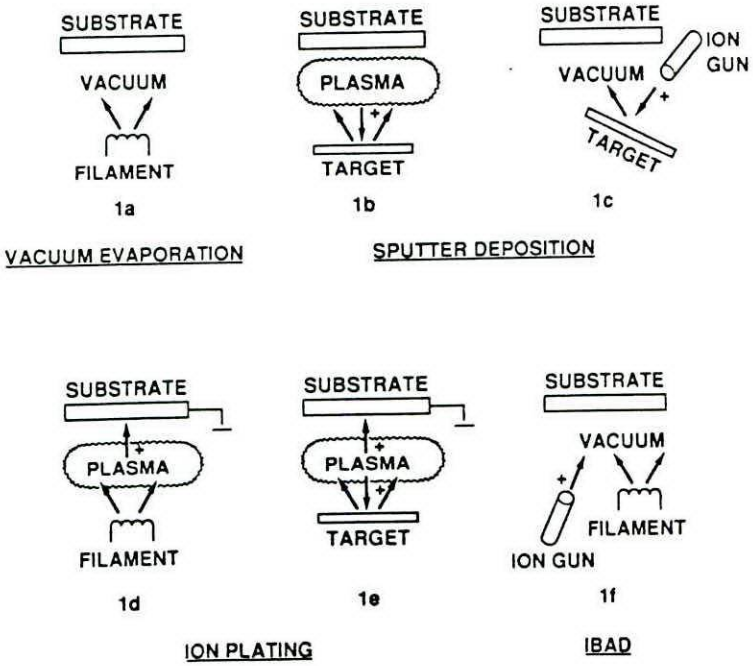

Figure 1: PVD processing techniques: 1a) vacuum evaporation, 1b) sputter deposition in a plasma environment, 1c) sputter deposition in a vacuum, 1d) ion plating in a plasma environment with a thermal evaporation source, 1e) ion plating in a plasma environment with a sputtering source and 1f) Ion Beam Assisted Deposition (IBAD) in a vacuum environment with a thermal evaporation source and ion bombardment from an ion gun.

* 1 nanometer (nm) = 10^{-9} meters = 10 Angstroms (A) = 10^{-3} microns = 0.04 microinches.

VACUUM EVAPORATION

Vacuum evaporation is a PVD process in which material from a thermal vaporization source reaches the substrate without collision in the gas phase (1). This means that there is no scattering during transport and the trajectory of the vaporized material is "line-of-sight". The vacuum environment also provides the ability to reduce gaseous contamination in the system to a very low level. Typically vacuum evaporation takes place in the pressure range of 10^{-5} Torr ** to 10^{-9} Torr depending on the level of gaseous contamination that can be tolerated. Figure 1a depicts a simple vacuum evaporation arrangement.

Evaporation and sublimation

The vapor pressure of materials is very dependent on the temperature. Materials that have a high vapor pressure over the solid, such as chromium, sublime. If the material must be molten before the vapor pressure is substantial the material evaporates. Materials that have a high vapor pressure at a relatively low temperature may be vaporized from a resistively heated source such as a filament or boat. For more refractory materials, the material is vaporized using a focused electron beam source. In either case the area of vaporization is rather small resembling approximating a "point source". When vaporizing large amounts of material the source may be replenished using wire or pellet feeds to keep the level of the evaporant constant.

In most cases evaporation of alloys of materials results in a change in composition since the alloying materials usually have differing vapor pressures and thus evaporate at differing rates. In some cases the alloy composition can be retained using "flash evaporation" techniques where small amounts of material are completely evaporated. In the case of evaporation of compounds the composition of the deposited material often differs from that of the starting material because of decomposition and loss of a portion of the more gaseous material i.e. oxygen from an oxide. Thus substoichiometric oxides are normally deposited by vacuum evaporation.

Other vaporization sources

In addition to evaporation and sublimation, other specialized vaporization techniques may be used in a vacuum. Arc vaporization is used to vaporize electrically conductive materials in a high-current low-voltage electric arc. This technique produces high vaporization rates with a high percentage of the atomic vapor being ionized. These ions are accelerated away from the arc and achieve a kinetic energy much higher than thermal energy. In the arc vaporization process molten globules are formed which deposit along with the atomic species. These globules are often detrimental to the properties of the deposit and various techniques are used to try to eliminate them. Laser vaporization (laser ablation) is used to vaporize compound materials and has found particular application in the deposition of high quality high transition temperature (high T_c) superconductor oxides.

Thickness and surface coverage

Since the thermal evaporation is from a point source and the flux has a cosine distribution around the normal to the surface the distribution of the deposited material is determined by

** Atmospheric pressure = 760 Torr. 1 Torr (mm mercury) = 10^3 milliTorr (mTorr). 1 mTorr = 7.5 Pascals (Pa) = 1 micron

the source-substrate distance, the angle of the substrate-source trajectory with the surface normal, and the angle of the substrate normal with the depositing flux. In order to increase the deposition uniformity the substrate is generally held in a moving fixture that randomizes the position and orientation of the substrate relative to the source during deposition. Another approach is to use multiple sources to produce an apparent large area evaporation source, although this approach makes thickness uniformity control more difficult.

The ability of vacuum evaporation to cover a surface depends on the surface topography. If the surface is smooth surface coverage will be good. However if the surface is not smooth, geometrical shadowing will prevent good surface coverage. Surface coverage can be improved by randomizing the deposition direction using fixturing that is moveable.

Advantages and disadvantages of vacuum evaporation

Some advantages of vacuum evaporation are:

- high purity materials can be deposited from high purity source material
- source of material to be deposited may be a solid in any form and purity
- line-of-sight trajectories and "point sources" allow the use of masks to define areas of deposition
- deposition monitoring and control are relatively easy

Some disadvantages of vacuum evaporation are:

- many alloy compositions and compounds can only be deposited with difficulty
- line-of-sight and point sources result in poor surface coverage on complex surfaces
- line-of-sight trajectories and point sources result in poor film thickness uniformity over large areas
- film properties depend on the "angle-of-incidence" of the flux of the depositing material
- fixturing with movement capability is necessary to improve surface coverage and thickness uniformity
- few processing variables are available for film property control
- substrate preparation is important to resulting film properties
- source material utilization may be poor
- high radiant heat loads may exist in the system
- the liquid source material may move thus changing the source configuration

Some applications of vacuum evaporation

Vacuum evaporation is widely used to form optical interference coatings, mirror coatings, decorative coatings, permeation barrier films on flexible packaging materials, electrically conducting films, and corrosion protective coatings.

SPUTTER DEPOSITION

Sputter deposition is the deposition of particles vaporized from a surface by the physical sputtering process (2). This PVD process is sometimes called just sputtering i.e. "sputtered films of --". Figure 1b and 1c show sputter deposition configurations.

Physical sputtering

Physical sputtering is a non-thermal vaporization process where surface atoms of a solid sputtering "target" are physically ejected by momentum transfer from an massive energetic

bombarding particle. Usually the energetic particle is an ion accelerated from a gaseous plasma. Electrically conducting materials may be sputtered in a direct current (DC) diode plasma configuration. Dielectric materials must be sputtered using a radio frequency (rf) sustained plasma. In the magnetron sputtering configuration a magnetic field is utilized to contain the plasma-generating electrons and produce a high plasma density near the target surface thereby increasing the sputtering rate. There are many sputtering configurations and often the sputter erosion pattern from the target is non-uniform requiring movable fixturing to obtain a uniform deposition over a substrate surface.

Sputter deposition may be performed in a vacuum using an ion gun or in a low pressure (<5 mTorr) plasma where the sputtered particles and reflected high energy neutral particles do not suffer gas phase collisions between the target and the substrate. Sputtering may also be performed in a higher pressure (5-30 mTorr) where energetic particles from the sputtering target are thermalized by gas phase collisions before they reach the substrate surface. The properties of the sputter deposited films depend strongly on the sputtering conditions.

Sputtering targets

The sputtering target is a solid surface and sputtering can be attained over a large area of a surface. Solid targets provide a long-lived vaporization source with rather constant and reproducible vaporization rates. Fabrication of large-area sputtering targets is often costly and the material utilization of the target is poor.

Reactive sputter deposition

By using a reactive gas in the plasma,the deposited material may be made to react to form a compound material. The reaction is promoted by "plasma activation" of the reactive species.

Advantages and disadvantages of sputter deposition

Some advantages of sputter deposition are:

- elements, alloys and compounds may be sputtered and deposited
- the sputtering target provides a stable, long-lived vaporization source
- the solid sputtering target may be mounted in any orientation
- in some configurations the sputtering target provides a large-area vaporization source that can be of any shape
- in some configurations the sputtering source may be a defined shape such as a line or a rod
- in some configurations reactive deposition may be easily accomplished because the reactive species are "activated" in a plasma (i.e. "reactive sputter deposition")

Some disadvantages of sputter deposition are:

- sputtering rates are low compared to those that can be attained in thermal evaporation
- in many configurations the deposition flux distribution is non-uniform requiring fixturing to randomize the position of the substrates in order to obtain films of uniform thickness
- film properties depend on the "angle-of-incidence" of the flux of depositing material
- sputtering targets are often expensive and material utilization may be poor
- most of the energy incident on the sputtering target turns into heat which must be removed

- in some configurations gaseous contamination is not easily removed from the system and gaseous contaminants are "activated" in the plasma thus making film contamination more of a problem than in vacuum evaporation
- in some configurations radiation and energetic particle bombardment from the plasma or sputtering target may change the film properties in an uncontrolled manner

Some applications of sputter deposition
Sputter deposition is widely used to deposit thin film metallization on semiconductor material, coatings on architectural glass, reflective coatings on compact discs, magnetic films, dry film lubricants and decorative coatings.

ION PLATING

Ion plating utilizes concurrent or periodic energetic particle bombardment of the depositing film to modify and control the composition and properties of the depositing film (3). Ion plating may be done in a plasma environment where ions for bombardment are extracted from the plasma or it may be done in a vacuum environment where ions for bombardment are formed in a separate "ion gun". The latter ion plating configuration is often called Ion Beam Assisted Deposition (IBAD) (4). Figure 1d and 1e show ion plating in a plasma environment. Figure 1f shows ion plating in a vacuum environment or IBAD.

Source of depositing species
The depositing material may be created either by evaporation, sputtering, or arc vaporization. The energetic particles used for bombardment are usually ions of inert or reactive gas, ions of the depositing material ("film ions") or ions of the reacting gaseous materials (e.g. oxygen or nitrogen).

Source of bias potential
Generally positive ions are accelerated to the depositing material due to a negative potential on the surface. This potential may be applied from an external source or be due to a "self-bias" on the surface. For electrical conductors such as metals, TiN, etc the applied potential may be DC. However if the film material is an insulator the applied potential must be rf in order to prevent a surface charge buildup which will cause the bombardment to cease. A self-bias can be caused to appear on the surface of a dielectric or electrically floating conductive surface by continuously bombarding the surface by high energy electrons.

Reactive ion plating
By using a reactive gas in the plasma the deposited material may be made to react to form a compound material. The reaction is promoted by "plasma activation" of the reactive species and the concurrent bombardment of the depositing material i.e. "bombardment enhanced chemical reaction". Materials such as TiN and SiO_2 are routinely deposited by reactive ion plating.

Film properties
The concurrent bombardment can be used to modify and control the properties of the depositing material. The most common film properties that are modified include: residual film stress, density of the deposited material and composition (stoichiometry) of deposited compound materials.

Surface coverage
Concurrent bombardment results in sputtering and redeposition of materials on surfaces that have a complex morphology. This effect, along with gas scattering at higher plasma pressures, can be used to give good surface coverage on complex surfaces such as ones having roughness or which have been patterned to form vias, metallization patterns, etc,

Other sources of concurrent bombardment
Concurrent bombardment of the depositing film can occur without a bias on the surface of the depositing material. For example, bombardment by the reflected high energy neutrals in low pressure sputter deposition and the ions accelerated away from the arc in vacuum arc evaporation can modify the film properties. Ion guns can be used to accelerate ions into a field-free deposition chamber.

Advantages and disadvantages of ion plating
Some advantages of ion plating are:

- in situ sputter cleaning of substrate surface
- surface coverage may be improved over vacuum evaporation and sputter deposition due to gas scattering and "sputtering/redeposition" effects
- bombardment may be used to modify film properties such as adhesion, density, residual film stress, optical properties, etc.
- film properties are less dependent on the "angle-of-incidence" of the flux of depositing material than with sputter deposition and vacuum evaporation due to gas scattering and "sputtering/redeposition" effects
- bombardment may be used to improve the chemical composition of the film material by "bombardment enhanced chemical reactions" and sputtering of un-reacted species from the growing film
- in some configurations the plasma may be used to activate reactive species, and create new chemical species that are more readily adsorbed and to aid in the reactive deposition process ("reactive ion plating")

Some disadvantages of ion plating are:

- there are many processing variables to control
- it is often difficult to obtain uniform ion bombardment over the substrate surface leading to film property variation over the surface
- substrate heating can be excessive
- under some conditions the bombarding gas may be incorporated into the growing film
- under some conditions excessive residual compressive film stress may be generated

Some applications of ion plating
Ion plating is used to deposit hard coatings on surfaces, adherent coatings on surfaces, optical coatings with high densities, and conformal coatings on complex surfaces.

SUMMARY

There are a variety of PVD techniques, each with many variations. Each of these deposition options has advantages and disadvantages. The choice of technique to be used to accomplish a specific coating task depends on a number of factors that must be evaluated for each situation.

REFERENCES

1. "Film Formation Methods" Chapter 6 in Coatings on Glass H.K. Pulker, Thin Film Science and Technology Series #6, Elsevier 1984
2. "Sputter Deposition Processes" Robert Parsons, Chapter II-4 in Thin Film Processes II, edited by John L. Vossen and Werner Kern, Academic Press 1991
3. "Ion Plating", Donald M. Mattox, Chapter 13, in Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions, edited by S.M. Rossnagel, J.J. Cuomo and W.D. Westwood, Noyes Publications, 1990
4. F.A. Smidt "Use of ion beam assisted deposition to modify the microstructure and properties of thin films" International Materials Reviews 35(2) 61, 1990

AN ELECTROPLATERS VIEW OF PVD PROCESSING

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For AESF SUR/FIN 92

Atlanta, Georgia

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ABSTRACT

This paper provides a comparison of electroplating and PVD processing from the viewpoint of a person who has been involved with the electroplating industry for the past 42 years and PVD processing for the past 12 years. During this recent 12 year period he has served as a manager of groups involved with both electroplating and PVD operations so he has had the chance to closely observe both technologies. After a brief description of each of the coating processes, comparisons are provided with respect to coating choices, deposition rates, properties, adhesion, costs and waste minimization. In addition, examples are provided to demonstrate that by combining the deposition technologies synergism can often be obtained. The conclusion drawn from these comparisons is that both deposition technologies are viable processes and each has its own particular benefits/drawbacks.

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Introduction

Don Mattox, Technical Director of the Society of Vacuum Coaters, asked me to put this paper together for this session of AESF SUR/FIN 92. Don wanted a view from someone who has been involved with both electrodeposition and physical vapor deposition (PVD) technologies and he is well aware that I have worked both sides of the street on this issue. We can both remember the time when I firmly believed that the only worthwhile coating process was electroplating, while in recent years some folks have accused me of trying to phase out electroplating completely. Hopefully, this paper will show that I consider both processes to be quite viable and that both will continue to play important roles in the coating field.

By way of background I feel I should establish some credentials before embarking on the main body of the paper. I've been involved in the electroplating field since 1950, having spent the first nine years with a consulting firm (PAVCO, formerly Cleveland Supply Co.) that sold brighteners to the plating industry, and the remaining years with research and development laboratories including Republic Steel's Research Laboratory (1959-60), Battelle Columbus Laboratories (1960-62), Sandia Livermore Laboratory (1962-1980), and Lawrence Livermore National Laboratory (LLNL) (1980 to present). In 1980 with the move to LLNL, I assumed the responsibility for groups involved in both electrodeposition and physical vapor deposition processes. Therefore, since 1980 I have been very closely involved with both technologies from both a managerial and technical viewpoint, so I've had plenty of experience with both deposition technologies. I should also add that although most of my time has been spent with R & D laboratories, a number of projects that I've been involved with have been transferred to production, so my views are not just those of a research oriented person.

This review will be broken down into four sections:

1. A brief description of each coating process
2. Comparisons with respect to coating choices, deposition rates, properties, adhesion, costs, and waste minimization
3. Examples where the combined use of PVD and electroplating provided synergism
4. Summary

Description of Coating Processes

Electroplating and Electroless Plating

Electroplating is the deposition of a coating of a metal onto another metal or a non-metal by electrolysis. This is accomplished when metal ions are reduced to the metallic state and deposited as such at the cathode by use of electrical energy.

Electroless plating is a chemical reduction process which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent, and the subsequent deposition of the metal without the use of electrical energy.

Physical Vapor Deposition

Physical vapor deposition (PVD) is a process whereby a material in bulk form is atomistically converted to a vapor phase in a vacuum and condensed on a substrate to form a deposit. PVD techniques fall into three broad categories: evaporation, sputtering, and augmented energy. In evaporation, vapors are produced from a material located in a source which is heated by radiation, eddy current, electron beam bombardment, etc. The process is usually carried out in a vacuum (typically 10^{-5} to 10^{-6} Torr) so that evaporated atoms undergo an essentially collision-less line of sight transport prior to condensation on the substrate which is usually at ground potential (not biased). Sputtering involves positive gas ions (usually argon) produced in a glow discharge which bombard the target material thereby dislodging groups of atoms or single atoms which then pass into the vapor phase and deposit on the substrate. Augmented energy techniques have been employed in more recent times to improve the energy of the deposition process. These include ion plating (D.M. Mattox, U.S. Patent 3,329,601 [1967]), thermionic plasma, and formation of plasmas using hollow cathode discharge sources. Ion plating is a generic term applied to atomistic deposition processes in which the substrate is subjected to a flux of high energy ions sufficient to cause appreciable sputtering before and during film deposition. The ion bombardment is usually done in an inert gas discharge system similar to that used in sputter deposition, except that in ion plating the substrate is made a sputtering cathode. The substrate is subjected to ion bombardment for a time sufficient to remove surface contaminates and barrier layers (sputter cleaning) before deposition of the film material. After the substrate surface is sputter cleaned, the film deposition is begun without interrupting the ion bombardment. Variations in the ion plating technique have given rise to terms such as vacuum ion plating, chemical ion plating, bias sputtering and others which refer to specific environment, sources or techniques.

Comparisons

In this section the deposition technologies will be compared with respect to: coating choices, deposition rates, properties, adhesion, costs and waste minimization.

A. Coating Choices

Electrodeposition and Electroless Plating

Thirty-one metals can be plated from aqueous solutions as alloyed metals (1) and these are shown in Figure 1. Of these, about 16 are commonly plated and these are highlighted in Figure 1. Molybdenum and tungsten can be deposited from aqueous solutions as alloys but not as pure metals. Alloy electrodeposition extends the availability and applicability of coatings from aqueous solutions and about 9 or so alloys have commercial importance (1).

Some metals have been deposited from non-aqueous solutions, the greatest success being obtained with aluminum which is being done commercially. Electrolysis of molten fluorides has been used for preparation of coherent deposits of zirconium, hafnium, niobium, tantalum, chromium, molybdenum and tungsten. Of these, successful production scale has been attained with tantalum, niobium, molybdenum and tungsten, although at present these aren't commercially available.

Many platers also have the capability of doing electroless plating. The metals which are commonly deposited by this process include nickel, copper, gold, palladium and silver. However, the most important of the electroless plating processes from the standpoint of commercial utilization are electroless nickel using sodium hypophosphite and copper using formaldehyde.

Physical Vapor Deposition

PVD offers a much wider choice of coatings and substrates than offered by electrodeposition. As an example, Figure 2 shows the metals that have been deposited in our facility at LLNL and it should be pointed out that other coatings are even possible. Comparison with Figure 1 clearly shows the superiority of PVD in providing a much wider range of coatings. Furthermore, an almost infinite range of alloys and optical coatings can be produced by PVD processes. Also, since the substrate does not have to be conductive as it does with electroplating, almost, any substrate material can be coated via PVD processing.

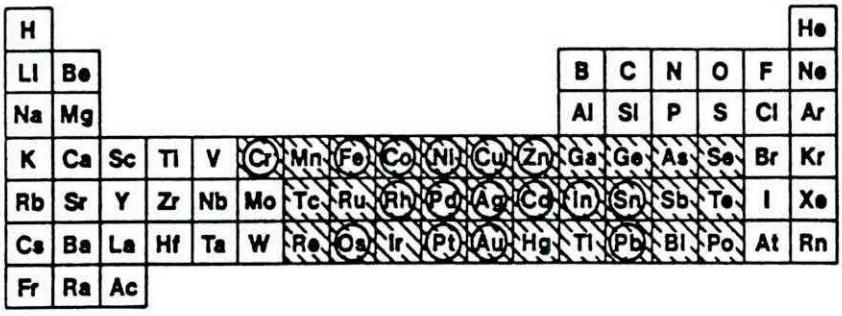


Figure 1: Periodic table showing metals which can be electrodeposited from aqueous solution. Diagonal lines show those metals which have been electrodeposited; circles are those most commonly used.

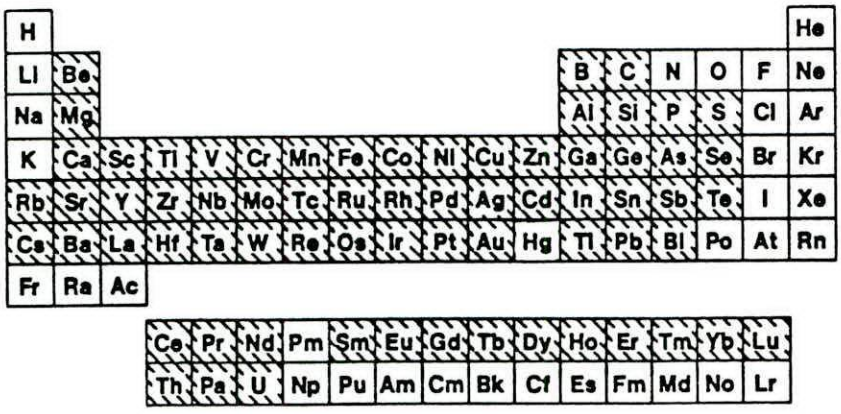


Figure 2: Periodic table showing those metals which have been deposited (diagonal lines) by PVD processes at LLNL.

B. Deposition Rates

Deposition rates for both electrodeposition and PVD processes overlap as shown in Table 1. This means that with specific PVD processes deposition rates can be as fast as those obtained with typical electrodeposition processes. However, very seldom are PVD processes used to produce thick coatings such as those used in electroforming, e.g., 10 mils (250 um), or greater. Most of the time, coating thickness for PVD films is expressed in Angstroms (Å) rather than the familiar term "mil" which is used by platers. For that matter it is my feeling that many platers don't even think in Angstroms (Å) since it is represents such a miniscule thickness. Table 2 provides some conversion factors for comparison purposes. Also, although deposition rates for the two technologies overlap, in many practical cases the deposition rates are faster for electroplating. Therefore, it can be quite difficult for a plater to deposit a coating of a few hundreds or thousands of Angstroms. For example, in the case of electrodeposition of nickel (assuming an efficiency of 95%), a thickness of 0.5 mil (12.5 um or 125,000 Å) is deposited in 23 minutes. This is a deposition rate of 5435 Angstroms/minute and means the plater has exactly 22 seconds to deposit a thickness of 2000 Å.

C. Properties

A wide variety of properties can be obtained with electrodeposits. This is done by using different plating solutions, by varying electrodeposition parameters, or by using additives. One good example is copper, which is deposited for numerous engineering and decorative applications. The range of properties obtainable for copper electrodeposits extends from strengths superior to full-hard wrought copper to properties equivalent to annealed pure copper. For data on the properties obtainable for various electrodeposits, the treatises by Safranek are recommended (2,3). The first edition (2) published in 1974 contains data reported from more than 1300 references while the second edition (3) published in 1986 contains information on 500 additional references.

Property data for PVD films are of a different nature since in most cases the films remain on their substrates and are not "free standing" as is the case with electrodeposits. For example, one can find a multitude of data on stress, hardness, and wear resistance of PVD films but virtually no data on tensile strength and ductility since the deposits are too thin for reliable measurement. Microhardness and scratch adhesion testing are the commonly used techniques for assessing the mechanical properties of thin PVD coatings (4). However, I am told by members of my PVD group at LLNL that property data for "free-standing" PVD films are being obtained and that as a function of time more data of this type will become available.

The structure of PVD films can be shown in three dimensional plots such as those developed by Movchan and Demchishin (Figure 3, Reference 5) and

Table 1

Typical Coating Conditions and Deposition Rates for Electroplating, Electroless, and PVD Processes

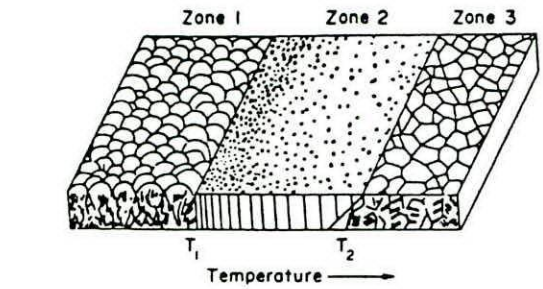
Deposition technique	Pressure (Torr)	Substrate temp. (C)	Deposition rate μ/min	mil/hr
Evaporation	10^{-7} to 10^{-5}	up to 250*	1.2-12	0.5-5
Sputtering	10^{-3} to 10^{-1}	up to 500*	0.012-24	0.005-10
Ion Plating	10^{-3} to 10^{-1}	up to 500*	1.2-12	0.5-5
Electroplating	ambient	10 to 100	0.4-180	0.15-75
Electroless plating	ambient	15-100	0.5-2.0	0.2-0.8

*Dependent on rate and material

Table 2

Conversion Factors for Coating Thicknesses

Angstroms	Microns	Platers Terminology	Inches
250	0.025	1 millionth	0.000001
10,000	1.0	40 millionths	0.000040
250,000	25.0	1 mil	0.001



	Zone 1	Zone 2	Zone 3
Metals	$<0.3\ T'_m$	$0.3\text{-}0.45\ T'_m$	$>0.45\ T'_m$
Oxides	$<0.26\ T'_m$	$0.26\text{-}0.45\ T'_m$	$>0.45\ T'_m$

Figure 3: Structural zones in PVD films prepared by electron beam evaporation. From Movchan and Demchishin, Reference 5.

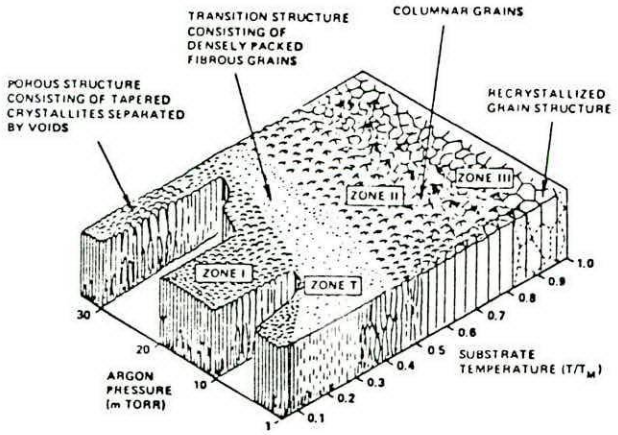


Figure 4: Structural zones in PVD films prepared by sputtering. From Thornton, Reference 6.

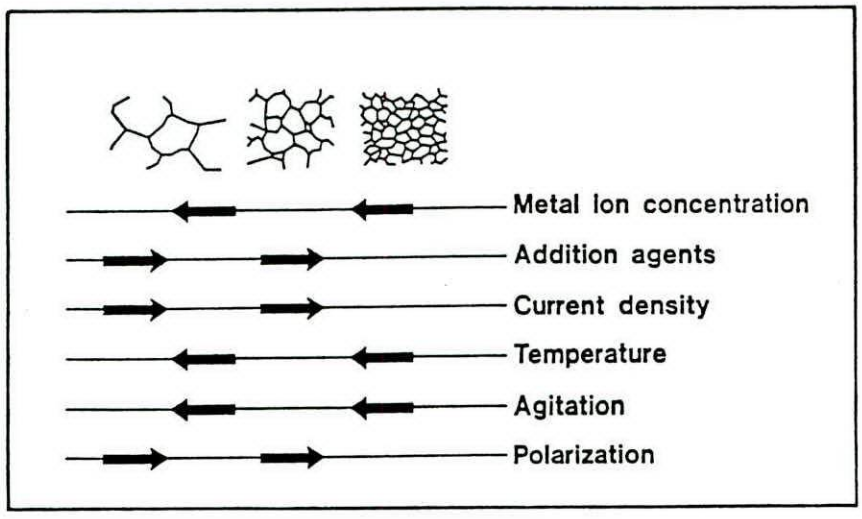


Figure 5: Relationship of structure of electrodeposits to operating conditions of plating solutions.

Thornton (Figure 4, Reference 6). Electroplaters aren't so fortunate since plating processes have more variables that influence structure, e.g., metal ion concentration, addition agents, current density, temperature, agitation, and polarization. Figure 5 pictorially shows how individual plating variables influence grain size of electrodeposits.

D. Adhesion

Excellent adhesion can be obtained with electroplated coatings on many substrates as attested to by a variety of quantitative tests such as ring shear, conical head and flyer plate. Table 3 lists a number of substrate materials and classifies them according to ease of coating with adherent electrodeposits. Those listed under the columns "easy to plate" and "special treatment" can be coated with adherent deposits that will not fail at the deposit-substrate interface. Those listed under the column titled "very difficult" often require extra steps such as heating or the use of augmented energy PVD techniques to provide good adhesion. When thick coatings are required, PVD and electroplating can be combined as discussed below.

With PVD films, adhesion has been reported to vary from poor to excellent (7-9). Sputtering is claimed to provide much better adhesion than the generally weak adhesion provided by evaporation. This is attributed to the higher energy of the deposition species in sputter deposition as compared to that of evaporated atoms (1 to 10 eV vs. 0.1 to 0.2 eV), References 10 and 11. By comparison, electroplating usually develops only a few tenths of an electron volt (11,12). With ion plating, the adhesion is reported to be excellent and better than with sputtering. Again, this is attributed to the highly energetic depositing ions (50 to 100 eV) as well as to the in-situ substrate pre-cleaning and the simultaneous deposition and substrate sputtering due to the continuous bombardment of the substrate during deposition (7,11).

Molybdenum can be used to show how the above generalized statements map with a specific substrate (Table 4). Adhesion of Be deposited on a cleaned Mo substrate via evaporation in a chamber evacuated to 10^{-5} to 10^{-6} Torr was only 31 MPa measured by a Sebastian tester with failure occurring at the interface between the coating and the substrate (13). With electroplating, adhesion of any coating would be no better than this unless special processing was used. For example, Table 4 reveals that good adhesion was obtained on Mo with processes that included hydrogen firing (e.g., gold strike and alkaline ferricyanide). Results with an acid etch/phosphonic acid process were considerably inferior. By comparison, copper deposited on Mo using magnetron ion plating followed by thick electroplating so that ring shear tests could be performed resulted in bond strengths of 216 MPa with failure occurring in the electroplated copper. With substrates such as Mo, Ti, and W the combined use of augmented energy PVD followed by electroplating can provide excellent adhesion of thick coatings without having to resort to severe etching of the substrates or heating after coating.

Table 3

Different Substrates Require Different Treatments to Provide Adherent Coatings

Easy to Plate	Special Treatment	Very Difficult
steel	stainless steels	titanium
copper	aluminum	molybdenum
brass	beryllium	tungsten
	magnesium	niobium
	plastics	tantalum
		glass

Table 4

Adhesion Data for Various Procedures Used to Apply Coatings on Molybdenum

Process	Deposit	Adhesion Results Sebastian MP_a	Adhesion Results Ring Shear MP_a	Location of Failure
Evaporation(A)	Be	31	-	Mo-Be Interface
Gold Strike/H_2 Fire /Electroplate(B)	Au	-	125	Au Deposit
Alkaline Ferricyanide Etch/H_2 Fire /Electroplate(C)	Au	-	90	Au Deposit/ Mo-Au Interface
Acid Etch/Phosphonic Acid/Electroplate(D)	Au	-	32	Mo-Au Interface
	Cu	-	37	Mo-Cu Interface
Magnetron Ion Plating(E)	Cu	69	216	Cu Deposit

(A) Be deposit was applied by vacuum evaporation in a chamber evacuated to 10^{-5} to 10^{-6} Torr. From Reference 13.

(B) This process included degrease in perchlorethylene, fire in dry hydrogen (< 2 ppm H_2O) at 1000°C for 10 minutes, immerse in a solution containing four parts NH_4OH (28%) and one part H_2O_2 (30%) for 8 to 10 seconds at room temperature, rinse in distilled water, gold strike to deposit 0.15 to 0.62 mg/cm² (0.08 to 0.32 µm), rinse in distilled water, fire in dry hydrogen at 1000°C for 10 minutes, electrodeposit to desired thickness.

(C) This process included degrease in perchlorethylene, immerse in a solution containing 300 g/l potassium ferricyanide, 100 g/l sodium cyanide for 10 seconds at room temperature, water rinse, electroplate to desired thickness, water rinse and then dry, hydrogen fire at 800°C for 4 hours.

(D) This process included degrease in perchlorethylene, anodic etch in chromic acid (10 percent by wgt) and 71 percent nitric acid (10 percent by vol) at room temperature and 15.5 A/dm² (1 A/in²) for 1 min, rinse, anodic treat in 50 percent aminotrimethylene phosphonic acid (ATMP) - 25 percent by vol, at room temperature and 15.5 A/dm² (1 A/in²) for 4 min, rinse, remove oxide film in chromic acid (10 percent by wgt) and 71 percent nitric acid (10 percent by vol) at room temperature for 1 min, rinse, electroplate to desired thickness.

(E) The magnetron ion plating process included sputter etching in vacuum, magnetron ion plating with 6 µm of copper and then electroplating to final thickness. Base pressure of the system was 5 x 10^{-6} Pa (10^{-8} Torr), etch power was 0.5 watts/cm², and bias power was 0.078 watts/cm² (but tapered to zero after deposition of about 20,000Å of copper).

E. Costs

This topic is not nearly as easy to quantify as those that have already been discussed. There is no doubt in my mind that PVD is more expensive than electroplating; the question is how much more expensive? My own experience plus information from two others will be discussed in the following.

Tom Beat, one of my colleagues who has spent his entire career in PVD and also works closely with outside firms, has provided some interesting information. He is aware of a disc manufacturer in the Silicon Valley who is convinced that to produce the same product (one million discs per month), PVD is ten times as costly as electroplating. Some of the items that contribute to this thinking are the following:

- for PVD a system costs $3 million and you also need a $1 million clean room
- a plating solution costs considerably less than $3 million and plating doesn't require a clean room
- with plating, the work could be processed using 16 hour days and a 5 day work week
- with PVD, the work would require 24 hour days and a 7 day work week
- with PVD every fourth shift would require down time for maintenance and changing of the cathode (deposition) source
- deposition sources are very expensive, e.g., $2000 for a PVD zinc source 6 inches in diameter by 0.625 inch thick ($439/lb compared to $0.72/lb for anode material for electroplating)
- in spite of the expense of PVD, it will be used to replace plating because plating requires 0.5 million gallons of water per day and water is becoming more and more difficult to obtain; also, plating would be replaced because of the hazards of working with and disposing of plating chemicals

Another source I've used is Dennis Koci, who is our resource manager at LLNL. Dennis has been closely involved with costing issues for electroplating and VPL operations during my 12 years at LLNL and he feels that the 10 to 1 ratio is probably a realistic number.

In spite of the above information, I don't know what the actual cost comparison ratio is between the two processes. Clearly, it is a function of many items that can vary from one installation to another. However, above and beyond the issue of capital equipment costs and maintenance which are very expensive propositions for VPL processing, it is evident that the simple issue of having a part coated is more expensive by PVD than electroplating. For example, a chamber has to be prepared, fixturing is often needed, pump down time is required, then the system has to be cleaned and re-configured for the next part. All this takes much longer than the time required for a plater to clean a part and complete the plating operation.

F. Waste Minimization

When comparing the two coating processes and discussing costs, one has to address the issues of waste disposal and waste minimization. There certainly is no question that PVD processing is considerably cleaner and offers savings via waste minimization that are not readily available via electrodeposition processes. Over the past five years we've spent over $500,000 in electroplating on waste minimization issues and this has certainly reduced operational costs because of eliminating or minimizing hazardous wastes which have to be handled and disposed. However, even with the added expense incurred with purchase, operation and maintenance of waste minimization equipment and the costs that still have to be incurred when disposing of hazardous plating wastes, the cost relationships between the two coating processes mentioned above still hold. A strongly influencing factor as already mentioned, which drives the cost of PVD processing is capital equipment and its maintenance. In our PVD facility, we could install only two, or perhaps three new systems for the $500,000 we've spent in plating waste minimization, and the maintenance costs in PVD would most likely exceed those that are required for our operation of waste minimization equipment in the plating facility.

Combining the Two Processes

Synergism can be obtained by combining electrodeposition and PVD. In a number of cases, better coatings and improved adhesion can be obtained when the two processes are combined. Also, for some applications, parts that could not be fabricated by either method itself could be produced when the two processes are combined. A number of references have appeared in the literature attesting to this and some examples will be discussed in the following paragraphs. For an overview and discussion of a variety of combined applications of the two coating processes see References 14-16. A listing of applications includes: metallization systems for hybrid microcircuits (17-19), copper on printed wiring boards (20), plating on difficult-to-plate metals such as W, Mo and Ti (16), a real time monitor for electroless nickel deposition (21), thick (1 mm) copper on glass (22), joining thin Be windows to stainless steel (14,23), fabrication of sputter cathodes by electroplating (24), electroforming parts with precision small inside diameter holes (25), plating on plastics (26), ceramic electronic substrates coated by PVD and reinforced by electroplating (27), molds for plastics, valves and nozzles (28), decorative coatings with various colors (29,30), and pens, wrist watches, jewelry and spectacle frames (31-33).

A. Plating on large molybdenum parts

The Precision Engineering Program at Lawrence Livermore National Laboratory was involved with the manufacture of precise, large-diameter, reflective optics for advanced laser systems by direct machining (34). Specific to

the topic of this paper were a number of Mo parts, including a 1.3 meter diameter ring shaped workpiece with a required form accuracy of approximately 250 Å rms. The parts were to be machined using a single-point diamond tool on a precision lathe under controlled machine and environmental conditions. Because diamond turning can be used successfully on face-centered-cubic metals (e.g., copper and aluminum) but not with Mo, (35-37) it was necessary to coat the Mo parts with thick (0.3 to 0.45 mm), adherent high-quality copper prior to final machining.

As discussed earlier, Mo is quite difficult to coat with an adherent deposit using conventional practices available to the electroplater. As shown in Table 4, the best adhesion was obtained when magnetron ion plating was used to provide the initial coating on Mo substrates. Although good results were also obtained with processes that included hydrogen firing (e.g., gold strike and alkaline ferricyanide), it would have been difficult to find a facility capable of hydrogen firing a part with a diameter of 1.3 m, and the potential warpage on a part of this size as a result of the high temperature (around 1000°C) required during firing could have proven disastrous to the close tolerances required.

B. Thick (1 mm) copper coatings on glass

This is an example of parts that could not have been fabricated unless the two technologies were combined. Thick (1 mm), adherent copper was needed on low coefficient of expansion glass to serve as a heat sink for a laser calorimeter. Another requirement was for 0.4 mm of copper on glass for an x-ray spectrometer system and lastly, diamond machinable coatings approximately 125 μm thick were sought for possible improvements in the optics of systems currently fabricated from metal. By applying an initial thin layer by magnetron sputtering or electron beam evaporation and then thick copper by electroplating, it was possible to fabricate the parts (22).

The conventional technology used by platers for metallizing nonconductors with stannous chloride/palladium chloride activation followed by electroless deposition prior to final electroplating is not acceptable for glass when thick coatings are required. With this process, deposits thicker than around 12.5 μm easily separate from a glass substrate.

The generally accepted criterion for adhesion between an oxide substrate such as glass and a metal film is that the metal must be oxygen active to react chemically with the oxide surface, forming an interfacial reaction zone (38). Metals such as niobium, vanadium, chromium, and titanium, which have a high negative heat of formation have a high affinity for oxygen. Deposition of one of these "glue" or "binder" layers by physical vapor deposition followed by a thin layer of copper without breaking vacuum produces an adherent base for thick electroplating.

The glass substrates were prepared by first fine grinding the surfaces to be coated with 3 μm particles of aluminum oxide followed by an etch in a six percent solution of nitric acid at 100°C. The glass was then placed in the vacuum coating chamber and preheated to 250°C for a minimum of eight hours. Next, the substrates were coated with a "binder" layer of 300 Å of either chromium or titanium using electron beam evaporation. Without breaking the vacuum between the coating steps, the binder layer was overcoated with 4000 to 5000 Å of copper. The parts were then electroplated with copper to final thickness, which in some cases was 1 mm. The electroplating was done at a current density that resulted in zero or slightly compressive stress. A part diamond turned after coating is shown in Figure 8.

C. Joining beryllium to stainless steel

Beryllium windows with a diameter of 0.96 cm and a thickness of 50 μm were joined to stainless steel anode housings for use in sulfur detector units which are compact x-ray tubes designed as a reliable fluorescence excitation source for use in a portable sulfur monitor. They contain a close coupled x-ray fluorescence spectrometer that uses silver L x-rays at 3 keV to excite characteristic x-rays of sulfur present in atmospheric aerosol particles. The sulfur monitor is unique in that the aerosol sampling and analysis are performed in the same unit with quantitative results available in real time.

The beryllium windows were joined to the stainless steel anode housings by using a combination of sputtering and electroplating. The thin Be discs were first coated with gold on their outer edges by sputtering, then placed in a pre-gold plated stainless steel tubular housing. All areas were masked except the sputter coated band on the Be and a companion area on the stainless steel. The Be foil was then joined in place using a thick nickel electroplate. Units fabricated by this combined PVD/electroplating process passed hundreds of hours of testing without degradation. By contrast, use of wet chemical methods, which had been successful with 250 μm thick Be windows (23), dissolved the 50 μm thick Be wafers. A completed unit is shown in Figure 9.

D. Reduced pressure deposition

Plating under reduced pressure was evaluated for both electroless nickel and electrodeposited copper systems. The objective was to reduce pitting of these coatings thereby further enhancing their usage for diamond turning applications. Cursory experiments with electroless nickel showed reduced porosity when deposition was done at around 500 Torr. Detailed experiments with electrodeposited copper at around 100 Torr provided similar results. More information on this work, which is also included in the technical program of SUR/FIN 92 can be found in Reference 39.

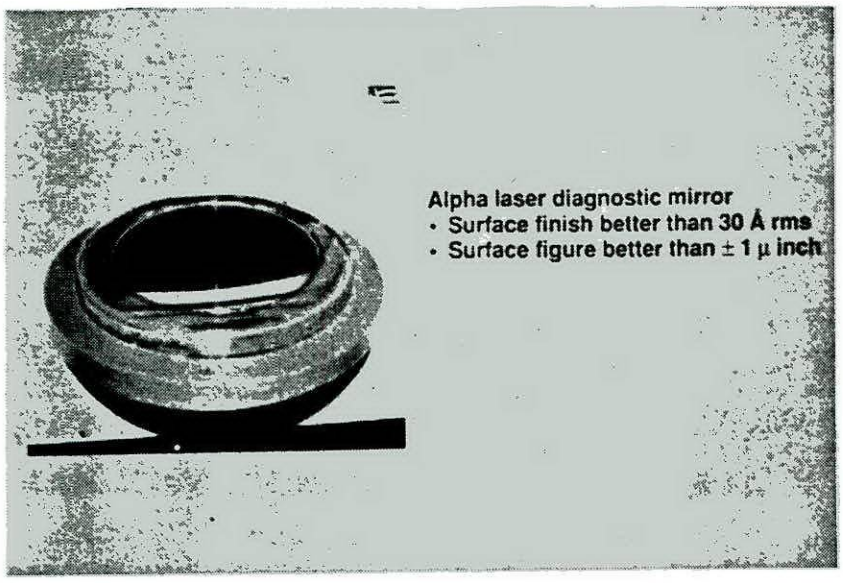


Figure 8: Diamond machined copper deposited on glass using the combined deposition processes. From Reference 22.

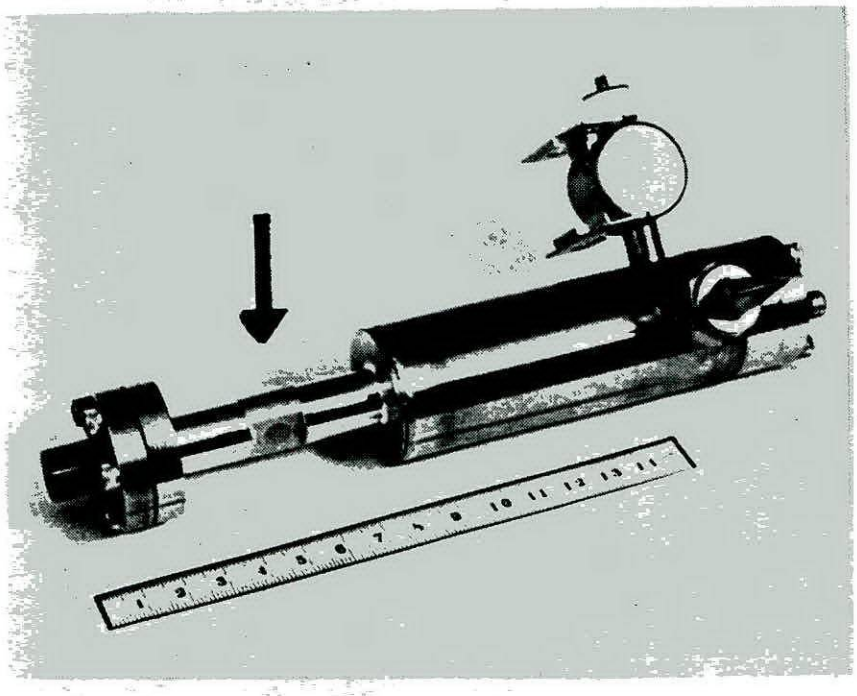


Figure 9: A beryllium window joined to a stainless steel anode housing by using the combined deposition processes of PVD and electroplating.

Summary

This paper has compared two deposition technologies, electroplating and physical vapor deposition. Each of these are extremely important, commercially viable processes and each has particular features that favor it in specific applications.

In terms of coating choices, PVD offers a much wider range than electroplating and PVD coatings can be applied to nonconductors. This isn't to say that electroplated coatings can't be applied to nonconductors, however, special processing is required. Although deposition rates overlap for both processes, thicker coatings (> 125 μm) are more likely to be produced by electroplating. PVD processes favor thin coatings (hundreds to thousands of Angstroms).

A wealth of property data are available for "free standing" electrodeposits but this is not the case with PVD films since these are typically too thin for reliable measurement. Data available for PVD films include stress, microhardness, wear resistance, and scratch adhesion resistance.

Adhesion can be excellent for both coating processes on many substrates. However, substrates such as W, Mo and Ti, with tenacious oxide films can be coated more adherently via augmented energy PVD processing than via electroplating procedures.

PVD processing is much cleaner than electroplating and offers definite advantages from a waste minimization viewpoint. However, even with the added expenses incurred for disposal of hazardous plating wastes and operation of waste minimization equipment, cost of PVD processing is higher than that of electroplating. Sources quoted in this paper suggest that PVD might be as much as ten times as expensive as electrodeposition.

Lastly, combining the two processes often results in synergism inasmuch as parts that could not be fabricated by other means could be produced when the two processes were combined. In other cases, better coatings with improved adhesion have been obtained. A number of examples and references are cited supporting combining the coating processes.

In summary, both PVD and electroplating are viable coating processes; each offers its own unique set of advantages and each has disadvantages. In a number of cases, combining the two processes has resulted in improved product, or parts that could not be fabricated by any other means.

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References

1. J. W. Dini, "Electroplating, Electroless Plating, and Electroforming", Proceedings SUR/FIN 90, Session T, 1193 (1990), American Electroplaters & Surface Finishers Soc.

2. W. H. Safranek, THE PROPERTIES OF ELECTRODEPOSITED METALS AND ALLOYS, American Elsevier Publishing Co., (1974)

3. W. H. Safranek, THE PROPERTIES OF ELECTRODEPOSITED METALS AND ALLOYS, Second Edition, American Electroplaters & Surface Finishers Soc., (1986)

4. P. J. Burnett and D. S. Rickerby, Thin Solid Films, 154, 403 (1987)

5. B. A. Movchan and A. V. Demchishin, Phys. Met. Metallogr. 28, 83 (1969)

6. J. A. Thornton, J. Vac. Sci. Technol., 11, 666 (1974)

7. N. S. Platakis and L. Missel, Metal Finishing, 76, 50 (July 1978)

8. J. E. Varga and W. A. Bailey, Solid State Technology, 14, 25 (1981)

9. P. R. Forant, Metal Finishing 77, 17 (Nov 1979)

10. H. K. Pulker, A. J. Perry, and R. Berger, Surface Technology, 14, 25 (1981)

11. J. J. Cuomo, J. P. Doyle, K. L. Saenger, C. R. Guarnieri and S. J. Whitehair, "High Density Amorphous Carbon Films and the Preparation of Diamond Membranes for X-Ray Lithography", APPLICATIONS OF DIAMOND FILMS AND RELATED MATERIALS, Y. Tzeng, M. Yoshikawa, M. Murakawa and A. Feldman, Editors, Elsevier Science Publishers B. V. (1991)

12. "Sputtering as a Deposition Process", Hohman Plating and Manufacturing, Dayton, Ohio, Bulletin SL-1002

13. A. K. Dua and R. P. Agarwala, J. Vac. Sci. Technol., A3 (6), 2612 (Nov/Dec 1985)

14. J. W. Dini, Plating & Surface Finishing, 72, 48 (July 1985)

15. J. W. Dini, Proceedings 1st International SAMPE Metals and Metals Processing Conference, Cherry Hill, NJ (August 1987)

16. J. W. Dini, Proceedings Third International Conference on Surface Modification Technologies, TMS, Neuchatel, Switzerland (1989)

17. P. L. Blessner, "Feasibility of Electroplated Gold for Hybrid Microcircuits", Bendix Kansas City, BDX-613-1740, (Oct 1977)

18. R. A. Hines and M. K. Raut, Proceedings AES 2nd Design and Finishing of Printed Wiring and Hybrid Circuits Symposium (Jan 1980)

19. W. W. Pcihoda and A. E. Walker, Electronic Packaging and Production, 15, 74 (June 1975)

20. A. Anderson, Plating & Surface Finishing, 68, 44 (Dec 1981)

21. K. K. Kanazawa and S. K. Doss, Plating & Surface Finishing 74, 52 (July 1987)

22. W. C. Cowden, T. G. Beat, T. A. Wash and J. W. Dini, Proceedings of the Electrochemical Society Symposium on Metallized Plastics: Fundamental and Applied Aspects, K. L. Mittal and J. R. Susko, Editors, (Oct 1988)

23. H. R. Johnson and J. W. Dini, Rev. Sci. Instrum. 46, No 1, 109 (Jan 1975)

24. J. W. Weed, W. K. Kelley, and D. M. Sanders, "Fabrication of Sputter Cathodes by Electroplating", Golden West Regional Conference, Santa Clara, CA. (April 1986)

25. W. K. Kelley, W. C. Cowden and G. E. Overturf, III, Proceedings AES Electroforming/Deposition Symposium (Jan 1983)

26. J. H. Lindsay and J. LaSala, Plating & Surface Finishing, 72, 54 (July 1985)

27. E. Flury-Frei, Galvano, 37, No 5, 54 (1990)

28. K. Reichel, W. Brandt and H. Mack, Galvanotechnik, 81, No 2, 426 (1990)

29. H. Erhart, Metalloberflache, 44, No 2, 59 (1990)

30. H. Erhart, Galvanotechnik, 81, No 4, 1216 (1990)

31. Anon., Galvanotechnik, 79, No 7, 2235 (1988)

32. Anon., Galvanotechnik, 80, No 6, 2059 (1989)

33. G. Kienel, Galvanotechnik, 80, No 6, 1937 (1989)

34. S. R. Patterson, "Development of Precision Turning Capabilities at Lawrence Livermore National Laboratory", UCRL-94719, Livermore, CA (June 1986)

35. B. Krauskopf, Mfg. Eng., 92, 90 (May 1984)

36. B. M. Hogan, "Microstructural Stability of Copper Electroplate", Proc. AES 71st Annual Technical Conference, (1984)

37. J. W. Dini, "Perspective on Plating for Precision Finishing", Proc. ASPE Spring Topical Meeting on Metal Platings for Precision Finishing Operations, Tucson, AZ (April 1991)

38. D. M. Mattox, Thin Solid Films, 18, 173 (1973)

39. J. W. Dini, W. C. Cowden, T. G. Beat, L. E. Ryan and W. B. Hewitt, "Plating Under Reduced Pressure", Proceedings SUR/FIN 82, AESF, Atlanta, GA (June 1992)

*** PAPER NOT AVAILABLE IN TIME FOR PUBLICATION ***

Production Techniques for Large-Area PVD Coatings

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There are various industrial applications using physical vapor deposition (PVD) processes for large-area coatings. Vacuum evaporation has been used for many years to produce mirror and solar control coatings. Sputtering is a well-known process for applying coatings to large sheets of architectural glass. Web materials of both plastic and metal are also coated by PVD in large area applications. This paper compares different PVD applications. Sputtering is especially of interest as a promising production technique that combines economical advantages with improved coating properties. Several products produced by these large area coating systems will be examined. The advantages and limitations of the processes and equipment will be discussed.

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*** PAPER NOT AVAILABLE IN TIME FOR PUBLICATION ***

High Volume Automotive-Type Aluminum Coating by Ion Vapor Deposition

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Ion vapor deposition (IVD) has been used for several years for the coating of high-strength steel, aluminum, and titanium alloy parts. Aluminum coatings for corrosion protection of numerous aircraft parts are now routinely applied in medium-volume batch IVD coaters. The properties and uniformity of IVD coatings have been demonstrated on many automotive, hydraulic, and electronic parts. The high volume required by these industries, however, has made it difficult to justify batch coating. A new continuous system now makes it possible to produce the volume of parts required for these applications. This paper will review the properties and potential for continuous IVD coating, using case histories developed for several emerging applications.

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"TiN Coatings for Wear Resistance and Gold-like Decorative Coatings"

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1. Introduction

Titanium Nitride (TiN) coatings have led the way for providing increased wear resistance and extended life of cutting tools, whether carbide inserts or high-speed steel. Where the earliest applications were for high temperature substrate materials (carbides) and chemical vapor deposition (CVD) was the process of choice, later developments in the physical vapor deposition (PVD) technology, especially in sputtering and cathodic arc deposition, made it possible to achieve similar improvements in performance for high speed steels and other heat sensitive metal substrates. Whereas the CVD process requires temperatures of about 1000°C to apply TiN, the PVD processes can apply the coating at temperatures of 500°C down to only 200°C, depending on the process chosen, and the application. As the deposition temperatures have decreased and the deposition rates have increased, the possible applications for TiN (and other hard coating materials) have expanded greatly.

Because of the gold color of TiN and other similar nitrides such as ZrN, HfN, and alloy nitrides such as TiZrN, applications for use as decorative coatings have developed in jewelry, writing pens, and other personal items. Because of their high hardnesses and relative chemical inertness, these materials are also protective coatings. TiN coatings typically have hardnesses of about 2200 kg/mm^2 (Vickers hardness), which is three times that of fully hardened tool steel. Still other coatings are being developed using alloy nitrides or carbides such as (TiAl)N (bronze) and TiCN (black) that are readily applied by PVD techniques and offer further options for wear and corrosion resistant decorative coatings.

2. Properties

TiN has excellent mechanical properties and finds many uses for wear resistance. As mentioned above, it has a hardness of about 2200 Vickers (VHN) compared to about 700 VHN for hardened M2 steel. It also has a low coefficient of friction (about .1) when sliding against steel. Its ceramic-like nature resists galling when used with steel in a sliding wear situation. In addition to good room-temperature properties, it retains its properties at much higher service temperatures. TiN is stable in air up to about 550°C, and has a melting temperature of 2950°C.

While the properties of the material are impressive, the performance of a coating depends on the deposition process and the substrate material as well. TiN is a good match for steels from the standpoint of thermal expansion coefficient, with a value of about 9 μm/m.°C compared to 10-15 μm/m.°C for steels. Other ceramic materials typically have expansion coefficients closer to half this value.

Since the compound is generally deposited in a reactive process, the composition can be varied somewhat, by controlling the amount of nitrogen available in the process. As the ratio of Ti to N gets closer to 1:1, the golden color deepens and the hardness generally increases. Other deposition parameters have important effects on the coating density, microstructure and internal stresses, which, in turn, effect the hardness, the adhesion and the corrosion resistance of the films.

3. Wear Behavior

The wear behavior of TiN coatings has been studied in recent years at many laboratories including BIRL. We have found outstanding properties when the coating-substrate system is optimized for best performance. Wear testing has demonstrated that TiN coatings can be very successful in enhancing rolling contact fatigue resistance of bearing steels [1]. Pure rolling tests have shown that very thin coatings (0.25 - 1.0 μm) can increase bearing life several fold. Whereas, a 4118 uncoated steel roller showed surface fatigue wear after 10 million cycles, a 0.25 μm TiN coating enabled the roller to run 60 million cycles with no evidence of wear or subsurface cracking. Thicker coatings of 2-5 μm (useful for cutting tools) performed poorly.

In other severe wear tests, involving combined sliding and rolling, the scuffing resistance of coated contact-elements was compared to that of uncoated elements under oil-lubricated conditions [2]. Dynamic test conditions were set so that scuffing failure loads of uncoated steels were quite low. The TiN coated steels generally remained intact to the load limit of the machine, at least one order of magnitude higher load than for the uncoated steel. Such results could be obtained with one or both elements coated, and again, the best results was for coatings that were 0.25-1 μm thick. The thicker coatings did not provide any benefit over the uncoated roller under the test conditions.

Similar tests with substrates of different hardnesses and coatings of different hardnesses (controlled by the deposition conditions such as substrate bias) showed the importance of matching the coating to the substrate for best result [3]. While the scuffing resistance of the hardest TiN film exceeded the machine-load-limit on an Rc62 (Rockwell hardness) steel, it

performed poorly on a softer, Rc45 steel of the same composition (52100). On the other hand, a relatively low-hardness TiN coating tripled the scuffing failure load of the softer steel and similarly enhanced the performance of the harder steel. The combination of hard coating and hard substrate was definitely best, but improvements could be made for both steels if the correct deposition parameters were used.

Analysis of the friction behavior of the TiN coated surfaces has also revealed interesting information about the scuffing behavior of the material. It has been established that the coating allows and sustains the formation of an oxide layer (tribo-chemical reaction products) that lowers the friction and resists scuffing. The uncoated surface cannot resist scuffing at the higher loads [4].

The corrosion resistance of these TiN coatings has also been the subject of investigation. The material itself is relatively inert at moderate temperatures in most common gaseous or liquid environments. Laboratory corrosion potential tests at BIRL and elsewhere [5] have shown that TiN coated steels are two to three orders of magnitude more resistant to corrosion in acid solutions than the uncoated steel. The true measure of its usefulness as a corrosion resistant coating is difficult to assess since its practical performance is limited primarily by our inability to make defect free coatings. Pin holes or other such defects tend to be the controlling factors in many cases, and the comparison given above is for general corrosion of the uncoated steel and pitting corrosion of the coated steel. Deposition parameters, especially substrate bias, which can effect microstructure and density also strongly influence the performance of these coatings.

4. Deposition processes

Today's PVD processes for depositing TiN fall under two general categories: evaporation (resistance, electron beam or cathodic arc), and sputtering. Within these categories there are many variations, but the processes that produce the high quality coatings generally incorporate substantial ion bombardment of the growing film and substrate. This ion bombardment, when properly controlled, produces highly adherent films with good mechanical properties. The ions may be from the evaporated species as in the arc process or as in ion plating processes, or they may be ionized argon gas atoms as in the case of most sputtering processes. This ion bombardment supplies energy to the film that cannot be made available by increasing the substrate temperature and it helps in densifying the microstructure.

All the processes have their strengths and weaknesses, which have defined the areas of application where they are most successful.

The ion plating process is capable of high quality coatings, of good density and good surface quality. A commercially successful process is, however, operated at a temperature of about 500°C, which limits some of its applications. Also, being an evaporation process, it is not as flexible as sputtering for the deposition of alloy nitrides.

The arc process is also capable of highly adherent coatings, and is more flexible in the types of materials that can be deposited. Two difficulties with the arc process are: (1) the development of what are called macroparticles in the coating and (2) the potential for excessive heating in sensitive substrates. The macroparticles are unreacted metal (Ti) in the form of micron-sized nodules. While this has not been a severe problem for some applications such as cutting tools, macroparticles pose problems for corrosion applications and for rolling and sliding wear applications.

The magnetron sputtering approach offers great flexibility in the range of materials that can be deposited and it can maintain low substrate temperatures (< 200°C). The adhesion and coating properties can be very good and the control of microstructure for corrosion applications is very promising. Recent developments in "unbalanced-magnetron" sputtering at BIRL [6] and other laboratories [7-11] have created a large amount of interest in improved microstructure control of sputtered films. Traditionally, the process is thought to be somewhat more expensive than the other two because of target costs and utilization, and the somewhat lower deposition rates. Developments in gas-flow control [12] have enabled rates of 0.5 μm/min. to be achieved with TiN coatings on steel. The evaporation processes generally have the potential for deposition rates an order of magnitude greater than this, but the optimum rate will depend on the properties required in the coating as well as the inherent evaporation capability.

5. Conclusions

TiN coatings (and other hard, highly colored compounds) have great potential for applications in traditional and non-traditional areas. The coatings are very adherent and can be applied to a wide range of substrate materials including metals, ceramics and polymers. Very thin coatings, on the order of a fraction of a micron to a few microns, can provide order-of-magnitude improvements in wear resistance and corrosion resistance. TiN coatings should prove very useful for bearings, sliding surfaces, forming tools, and other wear applications, as well as for decorative coatings with protective requirements.

Cost comparisons, however, must be done very carefully, since they are very application dependent and must take account of both

direct and indirect costs and benefits. The PVD processes can often be cost effective because of reduced pollution/clean-up problems and greater part yield and performance, even though the capital equipment may be more costly than for some traditional coating technologies. Continuing improvements to overcome the recognized weaknesses, make each of the techniques more competitive all the time and increase their range of applicability.

Acknowledgements

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References

1. T.P. Chang, H.S. Cheng and W.D. Sproul, **Surf. Coat. Technol., 43/44**, (1990) 699.
2. W.D. Sproul, T.P. Chang and H.S. Cheng, Presented at the AT/DCC meeting, October 28-31, 1991, Dearborn, Mi.
3. T.P. Chang, R.H. Krueger, M.E. Graham and W.S. Sproul, To be presented at Earthmoving Industry Conference, Apr. 7-8, 1992, Peoria, Il.
4. T.P. Chang, M.E. Graham, W.D. Sproul, and H.S. Cheng, To be presented at International Conference on Metallurgical Coatings and Thin Films, Apr. 6-10, 1992, San Diego, CA.
5. B. Matthes, et. al., **Surf. Coat. Technol., 49**, (1991) 489
6. W.D. Sproul, P.J. Rudnik, M.E. Graham and S.L. Rhode, **Surf. Coat Technol., 43-43**, (1990) 270.
7. N. Savvides and B. Window, **J. Vac. Sci. Technol. A, 4(3)**, (1986) 504.
8. D.G. Teer, **Surf. Coat. Technol., 39-40**, (1989) 565.
9. A.G. Spencer, K. Oka and R.P. Howson, **Vacuum, 38**, (1989) 859
10. S. Kadlec, J. Musil and W.-D. Munz, **J. Vac. Sci. Technol. A, 8(3)**, (1990) 1318.
11. W.-D. Münz, F.J.M. Hauzer, D. Schulze, and B. Buil, **Surf. Coat. Technol., 49**, (1991) 161.
12. W.D. Sproul, **Surf. Coat. Technol., 33**, (1987) 73.

*** PAPER NOT AVAILABLE IN TIME FOR PUBLICATION ***

Decorative and Wear-Resistant Coatings by PVD Processing

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The increased use of physical vapor deposition (PVD) follows innovations in film performances and higher deposition rates. A wide variety of metals, alloys and compounds are now deposited economically by PVD techniques onto a broad variety of substrate materials and shapes. Some decorative and functional coating applications lend themselves to a PVD-only approach, but finished products commonly combine a cost-effective mix of coating technologies--notably PVD plus plating. As PVD technologies evolve, opportunities emerge for improving profits and performance in established markets as well as for entering new markets. This paper will review existing PVD applications and contemplate future opportunities for plating and finishing.

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ION VAPOR DEPOSITION OF ALUMINUM

ABSTRACT

In the mid 1970's, McDonnell Douglas developed a process known as Ivadizing (I.V.D.), utilizing the Ion plating technique to apply a uniform, dense and highly adherent aluminum coating. Initial corrosion trials indicated that the Ivadizing process was a suitable alternative to Cadmium.

Since that early development work and with over a decade of service in the Aerospace industry, much has been learned both practically and technically about this process.

The purpose of this paper is to present some of those findings and discuss both the present and future applications for this coating.

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INTRODUCTION

For many year's, Electroplated Cadmium has been the most widely used coating on high strength steels in the Aerospace Industry. Cadmium gave not only good corrosion resistance (cathodic protection), but was cost effective.
There are some major technical drawbacks associated with Cadmium. These include hydrogen embrittlement of high strength steels (due to the plating process), exfoliation corrosion in the countersinks of aluminum alloys, ecology problems (toxic waste), and the solid metal embrittlement of titanium.

In recent years, the ecology issue has become one of the main factors in reducing the amount of Cadmium used in the industry. Tighter legislation imposed to control the disposal of toxic waste and reductions in the permissible level of Cadmium in effluent, has effectively increased the cost of this coating and made it less attractive to the plating shop.

Tests have shown aluminum coatings provide good corrosion protection, particularly in Chloride containing aqueous environments. Aluminum is anodic to steel and gives improved galvanic compatibility with aluminum alloys. Environmental corrosion tests of aluminum and Cadmium coated steel fasteners installed on operational military aircraft were reported to have shown better performance for the aluminum coated fastener. (Ref: Note 1)

A number of alternative processes are available for the application of aluminum coatings, namely metal spraying, cladding and electroplating, etc.. However, Ivadizing (Ion plating) affords the best control of thickness, superior adhesion, excellent "throwing power", low temperature application and good production throughput capabilities. Advances in the vacuum coating industry with rotary racks, specialized tooling and better pumping equipment, has made it much more competitive with the lesser tech coatings.

THE EQUIPMENT

The Ivadizer (coater) is a mild steel vacuum chamber (6' dia x 12') with an inside plating zone of approximately 5' x 10'. Removable stainless steel liners in the chamber help reduce pump down times by allowing the excess buildup of aluminum in the plating process to be removed at regular intervals. The chamber has a mechanical pumping system which consists of a three stage diffusion pump backed by a rotary-vane and booster pump. Correct choice of pumps and careful use of baffles, foreline traps or cold traps, limit the possibility of back migration or back streaming of oil vapour molecules into the chamber.

In addition to the mechanical system, the Ivadizer utilizes a cryogenic system. Briefly, cryogenic pumping is the freezing of gas or vapour out of a vacuum system onto a very cold surface. In this particular operation, the cryogenic pump is used to trap and hold water vapour.

Various racks and fixtures are available to transport work to and from the coater. These dollies are composed of a simple framework with a rail to support the rack (parts tray) and four main leg supports, each with air cushion pads. This facilitates easy movement of loads to and from the coater. The racks (parts trays) are positioned on rollers to allow the components to be loaded and unloaded into the chamber. Rotary pass thru's on the chamber allow the use of rotary rack and barrels to rotate work under vacuum during the coating cycle.

THE PROCESS

Cleaning - As in most metal finishing operations, preparation of the substrate is vital if good adhesion is to be achieved. Oil lubricants, grease or dyes, can be removed using chlorinated solvents or specialized soak cleaners.

In order to minimize surface contamination, and particularly in cases where rust or even scale is present, a dry blasting operation using pure aluminum oxide (150-220 mesh) is necessary prior to vacuum coating. Great care needs to be taken at this stage to minimize surface roughness or irregularities since this would be detrimental to the coating finish and corrosion protection. The components are loaded within 4-6 hours to reduce the possibility of surface contamination. Prior to loading, excess media is removed with dry compressed air.

Gas Cleaning - Once loaded, the vacuum chamber is pumped down to 10-5 torr (45 minute cycle). This allows sufficient outgassing of the chamber, removing previously absorbed gasses and vapours from the coated rack, fixture, and chamber shields. At this point the chamber is backfilled with an inert gas argon to 10 microns. A negative dc (1kv) potential is applied to the substrate (cathode). Positive Ions are produced by collisions between high energy electrons and gas atoms. Bombardment of the cathode (substrate) produces secondary electrons, hence, an avalanche effect is achieved. This process will continue until a normal glow discharge is achieved. This is characterized by the formation of a distinctive light pattern and an increase in current.

The positive ions are attracted to the substrate (cathode) dislodging substrate atoms and removing surface contamination (sputtering). This is not only effective at removing surface contaminants, but is responsible for the graded interface between the substrate and the coating, and hence, excellent

adhesion. The gas cleaning cycle lasts between 10-20 minutes, after which the atomically clean surface is ready for coating.

Coating - The evaporation source (anode) consists of seven intermetallic boron nitride or titanium diboride boats (crucible). Each crucible has an independent wire feed unit and when a high current is applied to the boat, (each crucible has a resistivity of 250-1000 micro-ohm/am), the resistive heat generated melts the aluminum wire which is subsequently vaporized.

Once evaporated, the aluminum atoms are ionized through collisions with high energy electrons or metastable gas atoms (peening ionization). These positively charged ion's are then attracted to and deposited on the negatively charged substrate (cathode).

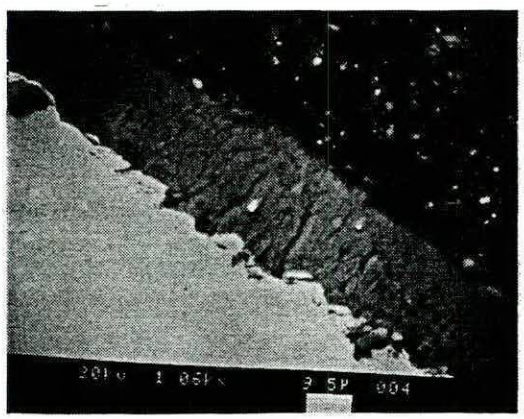
The speed at which the aluminum wire is fed to the crucible is carefully controlled, so the deposition rate offsets the sputtering rate to give efficient growth of the aluminum film and good adhesion.

The evaporation source is capable of traversing the length of the chamber at a controlled speed, hence, the coating thickness is dependent on the number of passes and speed during this operation.

COATING MICROSTRUCTURE

When investigated with a scanning electron microscope (SEM) the coating clearly shows a columnar structure with the grains extending outward from the substrate. The Ion plating process does help produce strong bonding between the individual columns, however, correct control of gas pressure, substrate bias, temperature and surface roughness (substrate) is necessary to achieve a low porosity coating with a uniform, dense structure.

Figure (1) Sem / Cross Section Aluminum Coating (1060 mag)



In the "as coated" condition, ion vapor deposited aluminum is very porous. This porosity is reduced by consolidating (burnishing) the coating using a glass media applied at a pressure of 20-30 lbs (psi). This compressing of the aluminum coating yields a more uniform, less porous and more durable coating. However, this is not capable of removing all evidence of microporosity.

To further improve corrosion protection, a chromate topcoat is applied. (Typically 200-250 Angstroms in thickness). This reduces porosity by "sealing" the coating and provides an excellent bond for a paint finish (barrier coat).

UNIFORMITY

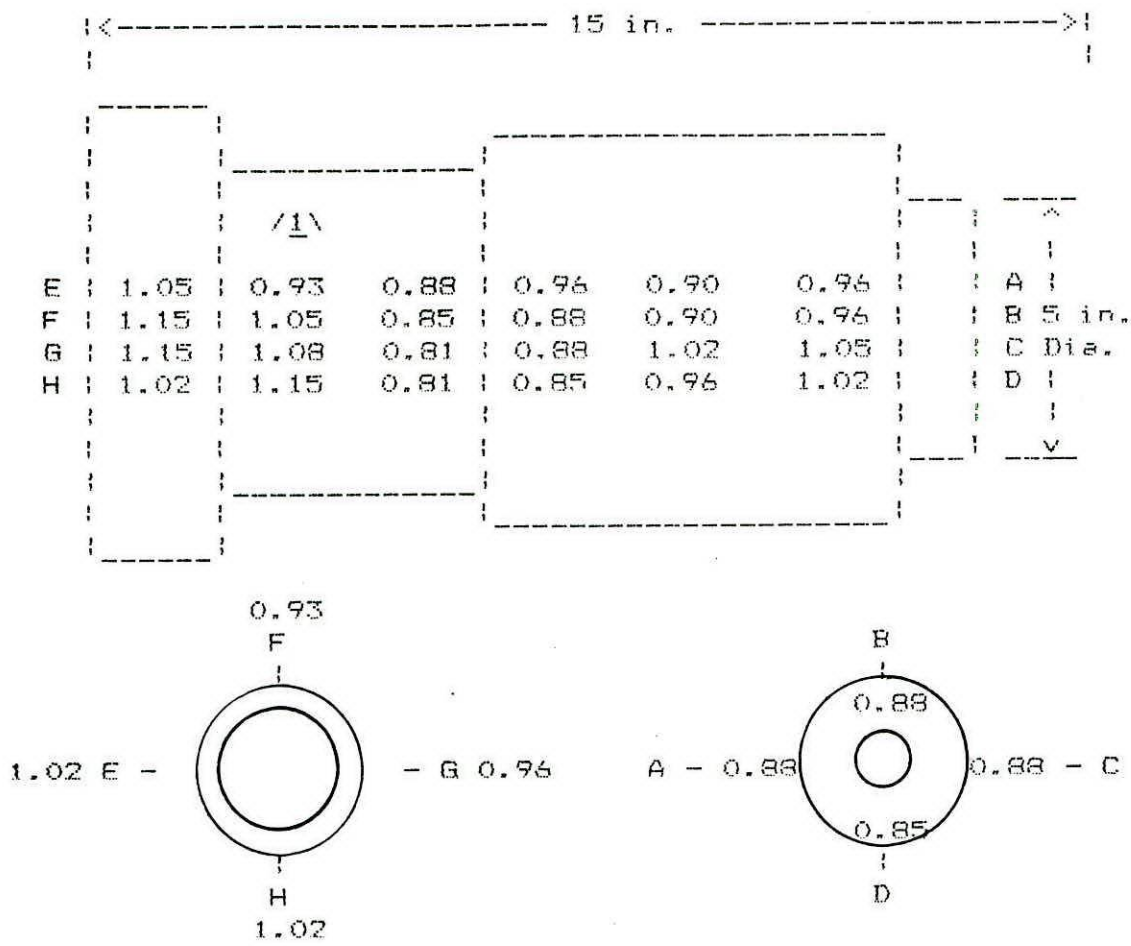
The main advantage with the ion plating process is thickness uniformity and excellent "throwing power". This is not strictly a line of sight process with the most complex of shapes receiving complete coverage in one coating operation. This has mainly been put down to the scattering of the metal vapour atoms through their numerous collisions between the evaporation source and the substrate. Also important is the sputtering process which is maintained throughout the coating operation, with metal atoms dislodged (momentum transfer) and re-deposited on the substrate.

Tests carried out by the author (B. Nevill) clearly showed the distance between the source and substrate is vital in providing good coverage. Typically, a distance of 12-15 inches from the evaporation source gave the best results with a 3 to 1 ratio (front to back) coating thickness in one coating operation.

Thru holes can be easily coated although it is difficult to control thickness. The coating will throw into bores to a depth equal to the diameter, although the coating thickness is non-uniform and tends to fade out quickly once the coating has reached half the diameter.

In a recent trial I was able to achieve full coverage in the I.D. of a 24 inch by 6.5 inch diameter tube (open both ends) in one operation. In practice, most complex shapes are turned through 180 degrees in the coating cycle. In many cases this is a cosmetic operation, allowing the movement of hooks and wire fixtures which would normally leave a mark or bare area.

Figure (2) IVD Aluminum Coating Thickness and Uniformity on a Cylindrical Detail



/1\ Coating thickness measurements taken at 90 degree Increments. All readings are in MILS.

Table I

IVD Aluminum Coating Thickness Variation
Throughout a Production Size Load of Fasteners

Fastener Number a,b	Coating Class	Coating Thickness (mils)	Average Thickness (mils)
1	3	0.44,0.55,0.47,0.34,0.62	0.48
2	3	0.77,0.44,0.45,0.62,0.59	0.57
3	3	0.77,0.35,0.44,0.71,0.56	0.57
4	3	0.65,0.35,0.47,0.44,0.35	0.45
5	3	0.87,0.30,0.52,0.44,0.47	0.42
6	3	0.66,0.46,0.54,0.61,0.40	0.54
7	3	0.37,0.32,0.53,0.43,0.58	0.45
8	3	0.61,0.39,0.31,0.30,0.55	0.43
9	3	0.36,0.44,0.50,0.33,0.37	0.40
10	3	0.46,0.58,0.38,0.38,0.38	0.44

a. Fasteners randomly selected from production size run of 150 lb of fasteners/barrel.

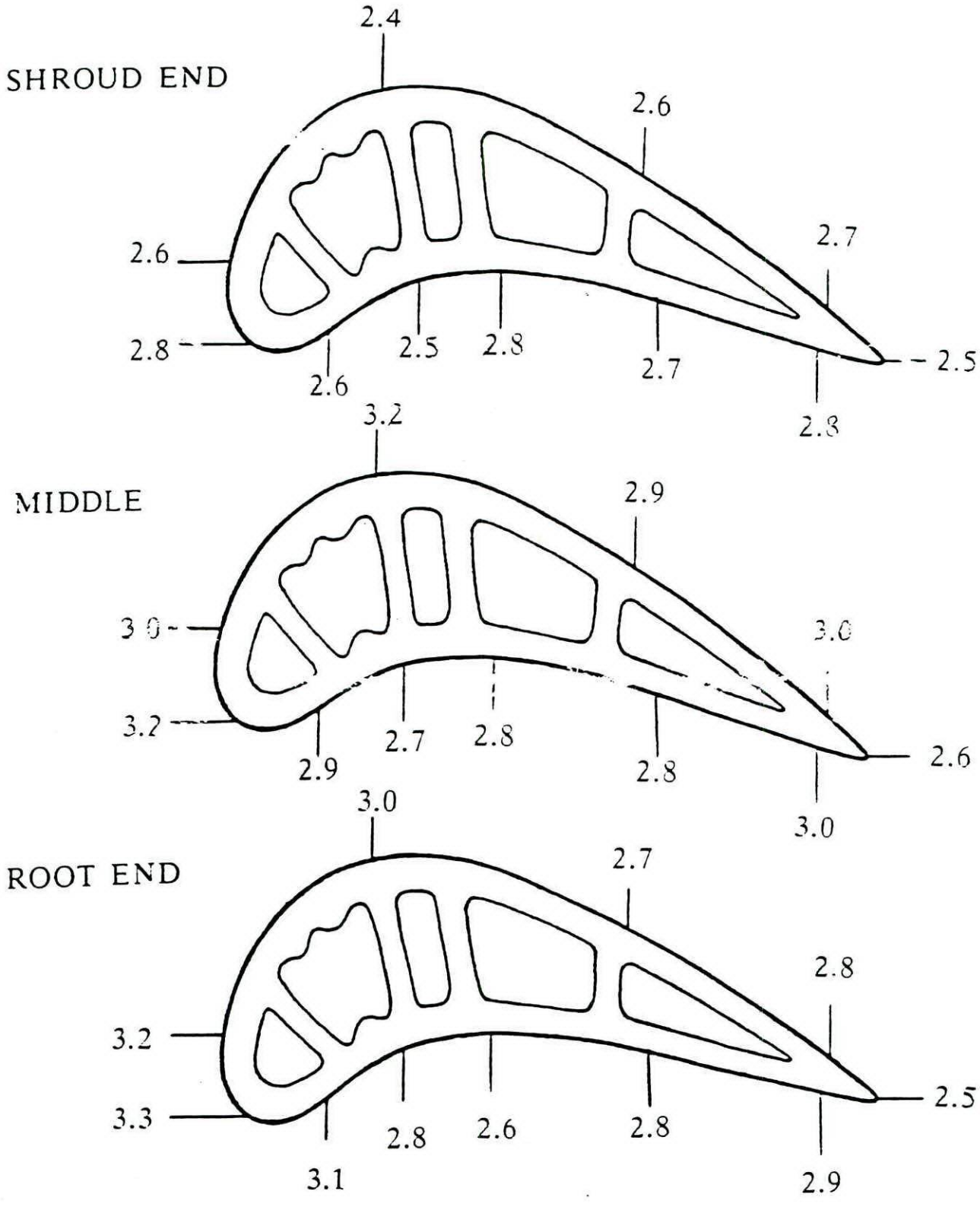
b. Hexagon head fasteners are 3/8" diameter x 2.7" long.

Figure (3)

Turbine Blade (Cross Section)

Figure (3)

COATING THICKNESS DISTRIBUTION



X0.001 INCH

CORROSION PROTECTION

Many evaluation programs have been carried out, covering the corrosion protection afforded by the I.V.D. process. Typically, these have included neutral salt spray, acidic salt fog, galvanic coupling, synthetic seawater tests and outdoor exposure. It is not my intention to reproduce the extensive data already published by McDonnell Douglas. However, the aluminum coating does tend to act sacrificialy, particularly on steels where the aluminum is anodic. In a recent salt fog trial, steel samples coated with I.V.D. aluminum exceeded 2,000 hours before showing signs of white corrosion. (Coating thickness 25 microns, Type I) A similar trial in seawater was also successful with the I.V.D. coating providing excellent corrosion protection (once chloride had formed on the surface).

Particularly important in most aerospace applications, is preventing galvanic corrosion from dissimilar metal contact. In a recent trial, I.V.D. coated steel reduced the corrosion rate of 7075 (alloy) when coupled and immersed in an aqueous environment. The 7075 alloy acts as the anode in the galvanic cell.

It can be concluded that I.V.D. aluminum does provide equal and in many cases, better corrosion protection than Cadmium in aqueous environments. The degree of protection depends on coating thickness and the level microporosity. Corrosion protection is increased still further with the addition of a chromate topcoat and in many cases, a barrier coat (paint).

Table II

MIL-C-83488

Class	Thickness	Salt Spray In Hours	
		Type I	Type II
Class 1	25 Microns	504	672
Class 2	12.5 Microns	336	504
Class 3	7.5 Microns	168	336

Type I: without chromate conversion
Type II: with chromate conversion

MECHANICAL FATIGUE PROPERTIES

Since the Ion plating process has no possibility of evolving free hydrogen, it is not necessary to perform lengthy embrittlement relief cycles after coating (typical in the more conventional coating techniques). This has also been the major factor in reducing the problems of stress corrosion cracking. McDonnell Douglas reported no signs of post hydrogen embrittlement or stress corrosion cracking of I.V.D. aluminum coated parts in over 12 years of field service experience. (Ref: Note 1)

The excellent bonding of the coating at the coating/substrate interface and tight knit columnar structure help reduce problems with fatigue. This graded interface has also been important in reducing problems associated with differences in the coefficient of expansion between the coating and the substrate. Also important is the relatively low substrate temp during the coating cycle with typical temp ranging from 90-150 degrees Fahrenheit.

Table III

Effect of IVD Aluminum Coating on Substrate Fatigue Properties

Company	Substrate	Fatigue Test	Effect on Fatigue(a)
Pratt & Whitney (Ref. 27 & 36)	8-1-1-Titanium	High Cycle	None
	6-4-Titanium	High Cycle	None
	410 Steel	Peak Strain	Slight-Same as Nickel-Cadmium
Westinghouse (Ref. 28)	A276 Steel	20 KHz	None
	A276 Steel	20 KHz	
	403 Stainless Steel	20 KHz	
SPS Technologies (Ref. 32)	Steel	Tension-Tension	Slight-Same as "Bright" Cadmium
McDonnell Douglas (Ref. 60)	2024 Aluminum Alloy	6g Symmetric	None
Turbine Support (Ref. 61)	Steel	High Cycle	None

(a) "None" - Less than 3 percent reduction
"Slight" - Less than 5 percent reduction

Table IV

Tension-Tension Fatigue Test of IVD Aluminum and Cadmium Finished Fasteners

Bolt Description (a) and Test Loads	Cycles to Failure (b)		
	Bare	IVD	Cadmium
MS21250-04-018 per MIL-B-8831	135,400	173,000	83,000
Alloy Steel	102,000	109,400	114,000
(Maximum Load - 3,210 lb.	72,200	107,700	125,000
Minimum Load - 321 lb.)	118,800	90,400	128,000
	178,600	102,100	123,000
Average	121,500	116,520	114,600

(a) NAS 1271-16 alloy steel fasteners
(b) Test method - MIL-STD-1312, test no.1 - speed 8,000 cycles per min.

TORQUE / TENSION

The aerospace fastener industry have always been concerned with the problems associated with the installation of I.V.D. coated fasteners. Over the years, this led to the development of aluminum/teflon paints, particularly for application on interference fit fasteners.

Typically, a higher torque is required to install an aluminum coated fastener (versus Cadmium), due to it's higher coefficient of friction. However, this can be greatly overcome using a cetyl alcohol lubricant. Applied after the I.V.D. process, McDonnell Douglas reported a 70% reduction in torque required for a given tension load. (Ref: Note 1)

I.V.D. coated fasteners have been in service now for nearly 12 years with very few reports of any serious problems. Indeed, for most parts, the addition of a lubricant has been sufficient, without a need to change installation procedures, tools or hole sizes.

APPLICATION

The larger percentage of business is still in the aerospace sector, divided between commercial and military contracts. I.V.D. still dominates a large sector of the aerospace fastener industry and existing McDonnell Douglas contracts (large wing foils and landing gear, etc.), including various large missile contracts.

Currently, I.V.D. and paint is the prime coating used on all the integral components for the Patriot, Amraam and Lantirn projects, one of the growing areas of business for I.V.D.. Over the last 2 to 3 years, there has been less demand for the I.V.D. coating on fasteners, mainly due to the introduction of the aluminum/teflon paints. Costs and ease of application have been the main factors behind this, rather than technical problems associated with the I.V.D. coating.

More specialized area's include ferrite assemblies (part of a phased array radar system - Patriot) coated with I.V.D. aluminum for wave guide purposes. This has also been applied and proved successful in a similar wave guide set-up used in microwaves. The excellent electrical characteristics (conductivity) exhibited by the I.V.D. aluminum coating has been utilized for electrical bonding purposes and more recently for EMI, RFI shielding. This has led to the most recent development of the I.V.D. process, the coating of plastic/composite materials.

When combined with a barrier coat (paint), I.V.D. has provided both shielding and corrosion protection on a variety of electronic assemblies. Adhesion between the coating/ substrate interface on a plastic/composite material is not the same as a metallic substrate. However, by applying Faraday's law, the author has managed to achieve better bonding on the substrate/coating interface on non-conductors by accelerating the charged particles through a screen. However, these high energy Ion's can damage the substrate, hence, the time of gas cleaning and voltage have to be controlled closely. Work carried out between the Author (B. Nevill) and A. Rashidi (Boeing) on compressed moulded gloss epoxy (1/10" thick) yielded a coating capable of passing a zone 1a lightning strike test. (A primer and urethane base coating was also applied).

Other composite materials (particular fibre wound, yielding partial conductivity) were successfully coated for EMI, RFI purposes. In this case a screen was not used, but great care had to be given to substrate temperature and the pressure in the chamber, otherwise problems with outgassing, delamination and cracking of the substrate material would occur. With only a fine tuning of the process required, the I.V.D. coating of plastics/composites is fast becoming a developing market for the I.V.D. process.

used for the production of permanent magnets was samarium cobalt. However, in the early 80's, a new rare earth based material was introduced, namely NdFeB (Neodymium Iron Boron). This proved to be a cheaper and more powerful source of magnetic energy, however, one of the main disadvantages of this material (NdFeB) was its poor corrosion resistance, particularly in humid or corrosive environments. Standard plating techniques were not suitable, since hydrogen evolved on the surface of the magnetand resulted in a breakdown of the alloy surface and, hence, a poorly adhered coating layer. Also a reduction in the magnetic properties of the material (BH, max.).

Tests carried out by two leading magnet manufacturers showed excellent results for the I.V.D. aluminum in both climatic and corrosive environments. With no hydrogen evolved in the I.V.D. process, excellent adhesion was achieved, yielding a thin uniform coating. This was advantageous, since it minimized air gaps in the magnetic circuit.

A more recent development was the combination of ivadizing and hot isostatic pressing (hipping) as a possible alternative to the more conventional aluminizing process (pack cementation) used on turbine blades. Initially this was isolated to the large blades (LP Blades) for economic reasons. Tests carried out with a leading turbine blade manufacturer concluded that the final diffused coating, produced on a directionally solidified material (MarM002) utilizing the IVD/HIP process, did yield a coating of comparable thickness, structure and composition to the present aluminizing process. However, this is still in the development stage with more work necessary to make the IVD/HIP process more viable both technically and commercially.

CONCLUSION

The IVD aluminum coating (ivadizing) has proven itself both in the field and in the test laboratory as a viable alternative to Cadmium.

Development over the last 5 years have proven the versatility of this coating, leading to even greater possibilities for this process.

With more and more demanding applications and an even more need for a safer, cleaner environment, design engineers should not overlook the I.V.D. (aluminum) process.

REFERENCES

Note 1
D.E. Muehlberger and J.J. Reilly - The substitution of IVD Aluminum for Cadmium, October 1988.

Figure (1)
Prepared by MMA Laboratories, California.

Figure (2), Tables I.II.III.IV
Produced by kind permission of McDonnell Douglas Aircraft Company.

Figure (3)
J. Higgins - Evaluation report of the IVD/HIP process. Rolls Royce, Derby, England.