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THE NEW APPLICATIONS OF SPUTTERING AND ION PLATING

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ABSTRACT

The potential industrial applications of sputtering and ion plating are strictly governed by the unique features these methods possess. The outstanding features of each method, the resultant coating characteristics and the various sputtering modes and configurations are discussed. New, more complex coatings and deposits can be developed such as graded composition structures (metal-ceramic seals), laminated and dispersion strengthened composites which improve the mechanical properties and high temperature stability. Specific industrial areas where future effort of sputtering and ion plating will concentrate to develop intricate alloy or compound coatings and solve difficult problem areas are discussed.

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INTRODUCTION

The desired characteristics of the end product tend to dictate the selection of a particular coating method. Sputtering and ion plating techniques are rapidly becoming two of the most important and versatile methods for the application of thin films. In addition, as a thin film deposition technique sputtering is emerging as a unique fabricating technique for the manufacture of intricate mechanical components which otherwise would be difficult or almost impossible to fabricate by machining, casting or powder metallurgy techniques. The potential industrial applications of these deposition techniques are governed by the unique features these methods possess.

The outstanding feature of sputtering originates from the fact that the sputtering process is not regulated by classic thermodynamics and Gibbs' phase rule relationships. Equilibrium conditions are not pertinent to this process. As a result, a new potential is emerging for materials development. Coatings can be applied in all possible chemical relationships, from stoichiometric to non-stoichiometric. Virtually any material can be sputter-deposited on any substrate. In addition, there is a high versatility in controlling the many sputtering parameters. As a result the mechanical, chemical and metallurgical properties of the coating can be favorably developed and controlled. Because of the high versatility in the sputtering process, many industrial areas are turning to this method for applications which require films that are difficult or almost impossible to prepare by other means. Considering the many modes of operation and the high flexibility in materials selection to fabricate coatings by sputtering, the potential future impact on industry is really in its infancy.
Ion plating when compared to sputtering is a relatively new technique, and therefore the commercial potentials have not yet been fully recognized. It has two outstanding, and unique features. First, coatings deposited by ion plating, due to the high energy ion flux, are exceptionally adherent. Secondly, the process has a high throwing power which permits the coating of complex, intricate objects uniformly. The potential uses of ion plating are essentially derived from these two characteristics.

The objective of this paper is to describe the unique coating features of each deposition method and discuss the various aspects of how effective coatings can be developed depending on particular industrial needs. New application areas and future trends of sputtering and ion plating are illustrated with specific commercial applications.

DISCUSSION

Unique Features of Sputtering

The unique features of rf sputtering make it the most versatile of all the deposition methods used today. From an industrial point of view where sputtering is utilized for many applications, the following features are of greatest significance: versatility, momentum transfer, stoichiometry, sputter etching, target geometries - coating complex surfaces, precise controls, flexibility, ecology and sputtering rates.

1. Versatility. Virtually any solid material regardless of its chemical complexity can be sputtered in the same stoichiometry on practically any type of specimen. Alloys, intermetallics, inorganic compounds, glasses, ceramics, cermets, selected organics such as teflon (PTFE), polymides and cattle bone have been successfully sputter deposited.
2. Momentum Transfer. The sputtered atoms from the target are transferred by a momentum transfer process. The sputtered atoms are dislodged by impact evaporation as opposed to thermal evaporation. Sputtering will occur only when the actual energy of the bombarding argon ions transferred to the target surface exceeds the usual lattice binding energy of 3 - 10 ev. Sputtering does not depend on the vapor pressures of the constituent elements, and since there is no direct heating involved it is sometimes referred to as a "cold process."

3. Stoichiometry. When the sputtering parameters are carefully controlled, multicomponent solids can be deposited with the same chemical composition. The target is water cooled to avoid thermal evaporation as well as bulk and surface diffusion. Since during sputtering less than 5 percent of the kinetic energy of the bombarding ions go into the kinetic energy of the sputtered atoms, the other 95 percent goes into the target as heat.

4. Sputter Etching. Before applying the potential to the target for sputter deposition, the potential is first applied to the substrate for sputter cleaning and etching. The purpose is to clean the surface of contaminants, oxides and skin effects of cold working that may be produced by mechanical polishing. Most sputtering systems are capable of sequential substrate cleaning or etching or simultaneously etching while sputter depositing.

5. Target Geometries - Coating Complex Surfaces. The shape of the target can be adapted to the object to be coated. Therefore, the shape of the target depends on the object coating requirements. The most commonly used target configurations are planar and cylindrical, and they can be fabricated from one or several sections of different material compositions as will be discussed later. Irregular, complex surfaces can be coated (into
cavities and around corners) without rotation in one operation primarily for two reasons. First, sputtered atoms leave the target at all possible angles in respect to the specimen which is in direct line of sight with some portion of the target. Second, the sputtered atoms will be scattered in random directions by collisions with particles in the plasma, enabling sputtered atoms to reach surfaces that are not in direct line of sight with the target.

6. **Precise Controls.** Sputtering offers an extraordinary control in terms of deposition rate, film thickness, uniformity, density and film morphology. Tolerance requirements can be controlled to a millionth of a centimeter.

7. **Flexibility.** Sputtering offers many options of various parameter combinations such that the chemical composition of coatings can be controlled and the coating deposited in any desired ratio from stoichiometric to non-stoichiometric. In addition coatings with graded compositions, laminated layers, and dispersion strengthening effects (through insoluble additions) can be formed. These various compositional changes can be performed in a number of ways. In the system which has one sputtering target the target can be fabricated of several segments or layers consisting of different material compositions. It can be accomplished by using multiple targets simultaneously or sequentially. Still another method is by reactive sputtering where a reactive gas is introduced into the system.

8. **Ecology.** Sputtering does not create any disposal problems. The reason for this is that the entire process is carried out in a self-contained system under vacuum. Nothing is exposed to the environment during deposition.
9. **Sputtering Rates.** As with any other deposition method sputtering has a disadvantage in that the deposition rates are relatively low. The average rate is 0.0005 to 0.3 µm/min. Equipment improvements, however, are gradually yielding higher deposition rates. In specially designed high rate sputtering systems, rates up to 250 µm/hr. have been achieved. In order to increase the rate, efficient ways must be found to cool the target sufficiently with increased power input.

The low deposition rates have also certain advantages. For example, it does afford a high degree of film control. The slow rates have a tendency to form denser films as compared to higher rates.

**CHARACTERISTICS OF SPUTTERED FILMS**

Functionability of a coating, regardless of its intended use depends primarily on the degree of adherence, coherence and morphology. Sputtered coatings grow in a complex plasma environment. The coating adherence, coherence and morphology are directly affected by: (1) sputter etching or biasing the substrate, (2) kinetic energy of the sputtered species, (3) plasma conditions, and (4) substrate temperature and topography.

The strong adherence normally obtained with sputtered coatings can be attributed to the surface cleanliness and the relatively high arrival energies of the sputtered material. These energetic submicroscopic sputtered particles have certain activation energies which not only favorably affect the surface adherence, but also increase the cohesion between the sputtered particles. The strong particle-to-particle cohesion is responsible for the formation of high density films. The submicroscopic particle size is important both in compactability and final density of the coating as
well as strength. Strength is generally related to the final grain size; the smaller the grain, the stronger the compact.

Due to the aforementioned characteristics, relatively thin films in the 0.2 to 1 μm range can be used where previously thicker films were required. It can be implied that it is more important how the coating is attached to the surface than the volume of coating present. It is well known that stresses induce peeling and internal stresses in the film increase with film thickness. Therefore, in sputtered films which are usually very thin (<1 μm) the stress induced peeling effect is substantially minimized.

The growth morphology and the resultant properties of the coating are interrelated. A diverse range of coating morphologies and properties can be reliably produced by controlling the various sputtering parameters and the substrate condition. These morphological changes become especially important as the coating thickness increases. For example, a preferred crystallographic texturing such as columnar, equiaxed, or epitaxial can be obtained. The grain size can be substantially decreased, which consequently increases the density of the coating, by simply bias sputtering. One of the most obvious bias related properties of many coatings is the optical reflectance at ground potential, and the dull and matte appearance at bias potential. A detailed discussion of this subject is outside the scope of this paper; such a discussion is given in references 1-4.

SPUTTER COATING POTENTIALS

By sputtering not only can any material be deposited stoichiometrically onto almost any substrate, but it can be done in chemical proportions and relations not regulated by classic thermodynamics and phase interrelationships.
Our thinking has been guided by Gibbs' phase rule which established the propriety of relationships by equilibrium thermodynamics. The key to the sputtering process is that equilibrium conditions are irrelevant. Therefore, this process has the potential and capability of forming new materials which heretofore were not even imagined.

The many sputtering modes and configurations such as the type of potential applied (dc or rf); target fabrication, configuration and positioning, substrate positioning, multiple target utilization, type of gases used (inert or reactive), auxiliary electrodes and utilization of magnetic fields contribute to the extreme flexibility in coating preparation.

The most widely used sputtering mode is the planar rf diode configuration with a single sputtering target. The objective generally is to obtain stoichiometric, adherent coatings. Solutions to new, more complex problems are being sought with sputtering. Sputtering has the potential of developing new materials with certain advantageous properties. A great variety of unusual coating compositions can be obtained by simply fabricating special targets which may consist of several segments of different material compositions. From a practical standpoint, powders of different materials can be mixed in any ratio and hot pressed into a sputtering target of any size and shape. Alternatively a target can be constructed of multi-component segments of different materials such as shown in figure 1(a). The three segments may consist of materials such as ceramic, glass, or metal. During sputtering all three segments are co-sputtered simultaneously to yield a material with the desired properties. Another useful target fabrication technique is by layering of the target materials as shown in figure 1(b).
The mixture ranges from 100 percent ceramic to 100 percent metal by desired (volume) increments - target with a reversed composition gradient. This target configuration is especially useful in the manufacture of ceramic to metal as well as metal to plastic and plastic to ceramic seals. Ceramic to metal seals require a graded interface to accommodate the high strains created between the two materials which have dissimilar thermal coefficients of expansion.

Use of multiple targets simultaneously or sequentially can yield dispersion strengthened structures through insoluble additions or alternate layers of different materials. All these combinations have a tendency to improve the mechanical properties which are of special interest for high temperature applications. These include retention of strength and resistance to creep.

USES OF SPUTTERED COATINGS AND DEPOSITS

Sputtering is primarily used in thin film technology. However, with the increasing sputtering rates, the process is emerging as a technique for the manufacture of intricate mechanical components with improved mechanical strength properties. On the basis of the sputtering rate considerations two areas of application can be distinguished: (1) thin film technology and (2) thick deposits or self-supported shapes.

THIN FILM TECHNOLOGY. In the last ten years sputtering has rapidly spread not only in the mechanical area but continues to proliferate into practically all areas which require films that are difficult or impossible to handle by other means. Just a few areas where sputtered coatings are having an increasing impact are: corrosion, high temperature oxidation protection, coatings for sodium cooled nuclear reactors, reduction of
friction and wear, coated tool tips and cutting tools, solid film lubrication, decorative coatings, films for integrated optics, replicating techniques, solar cell development, biomaterials for surgical implants etc.

Of all the specific industrial areas the greatest sputtering activity is in microelectronics and microminiaturization, which is incidently also the first area which turned to sputtering. Sputtering has been used in this field for the deposition of metals, semiconductors, and insulators, for production of MOS (Metal-Oxide Semiconductor) electronic devices, hybrid circuits/printed circuits, magnetic oxides and ferroelectric oxides for computer memory applications. These are just a few examples of the very active and rapidly expanding use of sputtering in solid state electronics technology.

Several specific examples will illustrate how sputtered films function in the mechanical areas. When solid film lubricants such as MoS$_2$ are sputtered on sliding surfaces, only 0.2 µm thick films are required for effective lubrication in vacuum or dry air (refs. 5, 6). An endurance life evaluation is shown in figure 2 where sputtered MoS$_2$ films are compared to two other application techniques.

Wear resistant hard coatings such as carbides, nitrides and silicides can be directly sputtered on friction and wear surfaces. For example, bearings when sputter-coated with a duplex coating (0.1 µm thick underlayer of Cr$_3$Si$_2$ and subsequently with 0.6 µm of MoS$_2$ produce marked improvements in endurance lives over MoS$_2$ films directly applied as shown in figure 3 (ref. 7). Sputtering has been used for coating tool tips, cutting edges, and braking surfaces of brake drums, with hard carbides or nitrides to improve wear resistance. New coatings have been developed for wear
resistance and stability in sodium cooled nuclear reactors, particularly for core component applications. Special formulations of modified silicon carbide and other refractory carbides have been sputtered for airborne components such as first stage compressor blades. These components operate in severe environments and have to be protected from corrosion, oxidation, erosion, and abrasion (ref. 8). Films for integrated optics with the objective of forming a complete optical circuit are being developed. Coating biological materials such as dried lung tissue with Au or Au/Pd films for scanning electron microscopy investigations has been accomplished. Sputtering is selected here because of the absence of excessive heating during the coating procedure without altering the surface morphology. Teflon PTFE (polytetrafluoroethylene) has been successfully sputtered with excellent adherence to metal, glass, paper and wood surfaces. Figure 4 shows, hypodermic needles used for cataract studies sputter coated with a 0.1 µm thick PTFE film. An interesting application is the sputter coating of cattle bone on metallic prosthetic devices for use in surgical implants as hip bone replacements (fig. 5, ref. 9). The sputtered bone film promotes bone growth and attachment to living bone.

THICK DEPOSITS AND FREE STANDING SHAPES. With the improvements in the sputtering equipment and especially with the development of high rate sputtering systems, rates up to 250 µm/hr have been achieved. This has been primarily accomplished with some metals sputtered by dc (refs. 10, 11). For sputtering to be a viable fabrication technique, the sputtering rate becomes a prime consideration from an economical standpoint, especially when one has to consider the deposits as thick as a centimeter. The relatively new sputter fabricating technology has basically
generated two types of products: (1) thick coatings (>25 µm) and (2) free standing shapes such as tubing, permanent magnets, laser mirrors and rocket thrust chambers, as shown in figure 6.

Thicknesses up to, but not limited to 0.63 cm have been achieved. Very intricate inner and outer cylindrical structures with coolant passages for thrust chambers are presently developed as illustrated in a cross section in figure 7. Specific mechanical, chemical and metallurgical characteristics are developed in these structures during the sputter-fabricating process.

CHARACTERISTICS OF ION PLATING

Ion plating is a high energy deposition method which differs from sputtering in that the coating material is evaporated into the glow discharge where it is partially ionized and subsequently accelerated toward the specimen by an electric field. Basically, ion plating has a diode configuration. The object to be plated is the termination point for an electric field which exists between the evaporation source (anode) and the work piece (cathode). In ion plating the specimen to be coated is the cathode, while in sputtering the substrate is generally the anode. The mean energy for a neutral particle generated through sputtering is in the range 10-40 eV, whereas in ion plating depending on the applied dc potential the energy of the impinging ions may be from 50 - 5000 eV. Ion plating is essentially the only coating technique where a potential (3 - 5 kV) can be applied directly across the specimen and the evaporation source.

Ion plating has two outstanding features which make it far superior to any other deposition method used today. Ion plated coatings have exceptionally strong adherence, coherence, and are fully dense. These
characteristics are achieved by sputter etching the surface, using high kinetic energy (50 - 5000 eV), and an amount of the ionized evaporant and surficial heating effects which accelerates diffusion and facilitates surface reaction. As a result of the aforementioned factors a graded-fused interface is generated. This type of interface not only provides a superior adherence but it also contributes to improved mechanical properties.

The second outstanding characteristic of ion plating is the high throwing power which permits coating of complex intricate geometric objects with a uniform coating. The potential uses of ion plating are based on the exceptionally strong adherence, and the high throwing power provided to coat complex surfaces with a uniform film. Since the resultant films are fully dense only very thin films in the order of 0.2 µm are needed for most applications. The exceptionally strong adherence is attributed primarily to the formation of a graded-fused interface rather than an abrupt film-substrate interface. Mechanical properties of metals are also favorably affected by this type of interface.

Nickel and Inconel tensile and fatigue specimens were ion plated with a 0.15 µm thick copper and gold film. Typical load-elongation curves for nickel and Inconel specimens with and without the copper film are presented in figure 8. The ion plated specimens exhibit higher strength such as an increase in tensile and yield strength from 5 to 8 percent. Ion plating effects on the fatigue life are presented in figure 9 where a 0.15 µm thick film of copper or gold had provided a 23 to 27 percent increase in fatigue life respectively. These two examples clearly
illustrate the potential effects ion plated films can have on mechanical properties.

Not only metallic but also ceramic and plastic components can be coated with virtually any material that can be successfully evaporated without a change in chemical composition. Various components coated by ion plating are shown in figures 10(a) and (b).

When thicker films over 2 µm are formed, the coating morphology can be favorably changed by controlling the energetics of the process. For instance ion bombardment energies (≥500 eV) can suppress the formation of a distinct columnar structure.

USES OF ION PLATED COATINGS

The areas where ion plating is most widely used are in the mechanical and metallurgical fields (refs. 12 - 16). A number of specific industrial areas where these coatings have had their greatest impact are discussed below.

Surfaces which require protective coatings against oxidation, corrosion and sulfidation can be protected. For example film failure leads to the occurrence of localized corrosion, such as pitting or crevice corrosion or stress corrosion cracking. Ion plating offers a high potential to eliminate these effects.

Application of soft metal lubricating films (Ag, Au, Pb, etc.) to sliding and rotating mechanical components. These films offer a lower coefficient of friction and longer endurance than films deposited by other vacuum deposition methods as indicated in figure 11.
Other application areas include strike coats for electro-plating materials which would be otherwise very difficult or impossible to plate, ion plating of metallic surfaces to facilitate their joining by conventional soldering and brazing techniques, decorative coatings for jewelry, glass bottles or any type of novelty item. In the automotive and jewelry industry there are many applications where polymeric materials are being used as substitutes for metals. The plastics perform the structural function, and the metal coating disguises the plastic. Still others include impregnation of fiber or glass wool with a metal, sealing porosity and microcracks in metallic components and refinishing worn out mechanical components by material buildup such as aircraft pistons.

CONCLUSIONS

Sputtering and ion plating are discussed in terms of the unique features which these two methods offer in depositing coatings. The future uses of these coatings depend on the unique features of these coating processes.

In coating and fabricating technology, sputtering has yet unexplored potentials due to the fact that virtually any material can be sputtered in proportions and relations that are not regulated by equilibrium thermodynamics and phase interrelationships. Many sputtering modes and configurations are available which offer a great flexibility in developing coatings and thick deposits of any chemical composition from stoichiometric to non-stoichiometric. More complex coatings and deposits can be developed such as graded composition structures, laminated and dispersion-strengthened composites which improve the mechanical properties and high temperature stability.
Ion plating has two outstanding characteristics: the high-energy ion flux and the high throwing power. These two features make it possible to coat complex geometrical surfaces in one step with a uniform, adherent coating which has a tendency to improve the mechanical properties of the specimen.

Industrial areas where the use of sputtering and ion plating will be concentrated include the development of intricate alloys or compounds to solve difficult problems. Although sputtering and ion plating may not be a "universal pill," they offer two of the best alternatives to prior existing coating technology.

REFERENCES


A 100
B 80 8 - 20
C - 60 C - 40
D 40 D - 60
E 20 E - 80
F 100

ELECTRODE

(a) THREE COMPONENT.

CERAMIC, METAL,
% %
A - 100
B - 80 B - 20
C - 60 C - 40
D - 40 D - 60
E - 20 E - 80
F - 100

(b) CROSS-SECTION WITH LAYERING OF MATERIALS.

Figure 1. - Construction of sputtering targets.

Figure 2. - Endurance lives of MoS₂ films applied by various techniques.
Figure 3. - Endurance lives of 400C stainless-steel ball bearings with sputtered MoS₂ films on races and cage - with and without a Cr₅Si₂ underlayer.

Figure 4. - Hypodermic needles and protective housings with sputtered teflon.
Figure 5. Typical joint prosthesis.
Figure 6. - Sputter-fabricated cylindrical chamber.
Figure 7. - Fabrication of cylinders by sputtering.

Figure 8. - Load elongation curves during tensile tests.
Figure 9. - Effect of copper and gold ion plated films (1500 Å) on the fatigue life of nickel.

Figure 10. - Ion plated insulators and metal objects with metallic coating.
Figure 11. - Coefficient of friction of niobium sliding on Ni-Cr alloy with gold deposited by vapor deposition, and ion plating about 2000 Å thick (load, 230 g; speed, 5 ft/min; ambient temp, 10^{-11} torr).