NASA TECHNICAL MEMORANDUM

NASA TM X-73527

NASA TM X-73527

(NASA-TM-X-73527) SPUTTERING (NASA) 13 p N77-12236
HC A02/MF A01 CSCL 13H

Unclas
G3/31 56897

SPUTTERING

by T. Spalvins
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER to be presented at the
Twenty-fifth Symposium of the Mechanical
Failures Prevention Group sponsored by the
National Bureau of Standards
Gaithersburg, Maryland, November 3-5, 1976

E-8944

SPUTTERING

T. Spalvins
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Abstract: This paper primarily reviews the potential of using the sputtering process as a deposition technique; however, the manufacturing and sputter etching aspects are also discussed. Since sputtering is not regulated by classical thermodynamics, new multicomponent materials can be developed in any possible chemical composition. The basic mechanism for dc and rf sputtering is described. Sputter-deposition is described in terms of the unique advantageous features it offers such as versatility, momentum transfer, stoichiometry, sputter-etching, target geometry (coating complex surfaces), precise controls, flexibility, ecology, and sputtering rates. Sputtered film characteristics, such as strong adherence and coherence and film morphology, are briefly evaluated in terms of varying the sputtering parameters. Also described are some of the specific industrial areas which are turning to sputter-deposition techniques.

Key words: Sputtering; Thin films; Protective coatings

INTRODUCTION

Sputtering is a process where a surface, when immersed in a plasma such as an ionized inert gas, is bombarded with energetic particles that cause ejection of surface atoms. The heart of the sputtering process is essentially the disintegration of the target material under ion bombardment. These ejected sputtered atoms can be collected onto a substrate to form a film.

Using the sputtering process as a film deposition method is receiving an enormous amount of interest and acceptance. New ways of applying the sputtering process are constantly being found for those areas where the more conventional deposition methods can not solve the problems encountered. In addition, as a film-deposition method, the sputtering process is used in sputter fabricating intricate mechanical components which are difficult or almost impossible to manufacture by machining, casting, or powder metallurgy techniques. The sputtering process is also used as a universal, nonchemical etching technique - for example, sputter etching, ion milling, or micromachining.

Especially in the film deposition area, the unknown potential for sputtering originates from the knowledge that it is possible to prepare new multicomponent materials (such as new alloys and compounds in any

STAR Category 37

chemical proportions and relations) and also, if needed, to form a continuous compositional change or concentration gradient. Since the sputtering process is not regulated by classical thermodynamics and Gibbs phase rule relationships, one is not forced to remain within the framework of the rigid regulations. All of these unexplored features show that sputtering is really in its infancy; therefore, at present the potential future impact of sputtering on industry is inestimable.

The purpose of this paper is to acquaint the mechanical engineer with the potentials of the sputtering process, particularly with the physical rf-sputtering technique. The following sections on sputtering modes, unique features of sputtering, characteristics of sputtered films, and some practical applications of sputtered films are written in an introductory nature in order to bring out and emphasize the key features of the method and the resulting films. For more detailed information one is referred to Refs. 1 to 6.

SPUTTERING MODES

There are two basic types of sputtering, depending on whether the glow discharge plasma is generated by direct current (dc) or radiofrequency (rf) fields. To induce sputtering, a negative surface charge has to be built up on the target. Besides the two basic dc and rf diode-type techniques, the sputtering modes and configurations are also as varied as the number of sputterers in the field. All of these sputtering modes and configurations arise essentially from (1) the way in which plasma is created (dc, rf, auxiliary electrodes), (2) the target and substrate positioning and their geometrical configurations, (3) the number of sputtering targets in the system, (4) the type of gases used (inert or reactive), and (5) the utilization of magnetic fields. A few modes are dc diode and triode, rf and dc/bias, dc-rf combinations, reactive sputtering, and magnetron sources.

dc Sputtering

The simplest sputtering configuration is the dc diode type, which consists of two electrodes. The coating material is the target or cathode, and the specimen to be coated is the anode. When these electrodes are immersed in an inert gas (argon) atmosphere of 10 to 100 μm and a dc potential of 500 to 5000 V, is applied across the two electrodes, ionization of the gas occurs, and generates a glow discharge plasma. The positive argon ions are accelerated toward the target with a kinetic energy high enough to knock off or sputter atoms from the target surface.

The oldest, simplest, and least expensive method is dc sputtering. The limitations to this method are that only conductors and certain semiconductors can be sputtered. Nonconductors (ceramics, glass, etc.) cannot be sputtered by the dc method. The reason is that a positive charge accumulates on the target's surface and acts as a barrier to further ion bombardment and thus the sputtering process. This problem, however, can be overcome by using an rf potential.

rf Sputtering

In rf sputtering a high frequency potential in the low megacycle range is directly applied to the metal electrode behind the target. The target (an insulator) is bonded to the metal cooled electrode, thus forming a capacitive coupling. Since the rf voltage is applied to the target assembly through rf fields generating plasma, the sputtering current is controlled by the rf voltage. Efficient plasma generation requires frequencies above 10 megacycles, and the resulting rf diode sputtering system operates usually at the allowed band of 13.56 megacycles. The insulator surface in contact with the plasma is alternately bombarded by electrons and positive ions during each rf cycle. When the surface is positive it attracts electrons, when it is negative it attracts ions. Since the electrons in the plasma have a higher mobility than the ions, the electron current to the target surface is initially much greater than the ion current. The cathode acts as a diode and charges the coupling capacitor to the peak value of the rf input voltage and then attains a negative bias.

If a voltage greater than 500 volts is applied, the surface bias will be sufficient to accelerate ions from the plasma to an energy high enough to cause sputtering of the insulator. A simplified schematic of the sputtering process is shown in Fig. 1.

All rf diode systems use the previous mechanism which makes the technique a universally applicable. In addition to sputtering insulators, rf-sputtering can operate at lower argon pressures (1 to 5 μm) and attain higher sputtering rates than dc sputtering.

rf Sputtering with dc bias

Of the many possible sputtering modes and arrangements which are used today, rf sputtering with a dc bias will be described very briefly. Fig. 2 shows schematically and photographically a sputtering system which consists of two independently operated sputtering processes: rf sputtering (deposition) and dc sputtering (cleaning). The dc sputtering process is used strictly for cleaning or sputter etching metallic substrates before rf sputter deposition. The specimen is thus capable of sequential substrate cleaning or etching followed by sputter coating or simultaneously etching (biasing) while sputter depositing.

DISCUSSION

Unique Features of Sputtering

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

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, selected organics such as teflon (PTFE), polyimides, and cattle bone have been successfully sputter deposited.

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 by the bombarding argon ions transferred to the target surface exceeds the usual lattice binding energy of 3 to 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."

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

If the target is kept at a sufficiently low temperature to avoid evaporation and diffusion, the composition of the sputtered material will be identical to the composition of the target, even though the chemical components have different relative sputtering yields. Stoichiometry in the sputtered coating is retained because the component having the highest sputtering yield cannot diffuse from the bulk to the surface as fast as it is removed by sputtering. Following this, the lowest yield component will be sputtered along. Very soon a steady-state condition is reached in which the material is transferred from the target to the substrate in the same composition.

An important property in sputtering is the sputtering yield which is defined as the number of atoms ejected from the target per incident ion. Carbon has the lowest sputtering yield, less than 0.1 atom per ion, while silver has the highest, 2.7 atoms per ion. Sputtering yield, which is synonymous with sputtering rate, will be discussed separately in the last section.

Sputter-etching. - Instead of applying the potential to the target, the potential is applied to the substrate to induce sputtering, which is essentially reverse sputtering. Before the substrate is sputter deposited it is sputter etched. 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 of simultaneous etching while sputter depositing.

Target geometries - coating complex surfaces. - Targets can have any size and shape such as planar, cylindrical, hemispherical, or some other suitable configuration. It can be made from one material or several sections of different material composition. Planar targets (12.7 to 20.32 cm diam.) are the most widely used. When such targets are sputtered, atoms leave the target at all possible angles as shown in Fig. 3. As a result, most of the specimen surface is in direct line of sight with some portion of the target. Also, because sputtering in a plasma occurs at relatively high pressures (5 to 25 μm), the mean free path of the sputtered atoms is relatively short (<1 cm). Thus, the sputtered atoms will be scattered in random directions by collisions with particles in the plasma; such scattering enables sputtered atoms to reach surfaces that are not in a direct line of sight with the target. As a consequence, irregular, nonsymmetrical surfaces can be coated in cavities and around corners without any rotation in just one operation.

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.

Flexibility. - Sputtering offers many options of various parameter combinations. As a result, the chemical composition of the coating can be controlled in any desired ratio from stoichiometric to nonstoichiometric compounds. In addition, graded compositions, laminated structures (composites), dispersion strengthened structures, and insoluble additions can be formed. These various compositional changes can be accomplished in a number of ways; for example, multitargets can be used where controlled mixing of materials is performed by sputtering from different targets or by reactive sputtering where the flow rate of the gases carrying one of the reaction product constitutents is carefully controlled.

Ecology. - Sputtering does not create any disposal problems.

Sputtering rates. - Sputtering has the disadvantage that deposition rates are relatively low. The average rate is 0.005 to 0.3 μm/min. However, equipment improvements 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 sputtering rate (yield) to a first approximation can be related to the type of the material being sputtered and the sputtering parameters (bombarding ion flux density, angle of incidence, gas pressure, target and substrate temperature, etc.). The general trend as to how the sputtering parameters affect the rate are shown in Fig. 4. The rate increases with rf-power input to a maximum value and then falls off. Above the ion bombarding energy of ∿7 keV, there is no gain in sputtering yield. An increase in spacing between the target and the specimen decreases the deposition rate. Increases in the target and substrate temperatures also decrease the deposition rate. Although an increase in the gas pressure initially increases the sputtering rate, it eventually causes a decrease in the deposition rate because of a decrease in the ion mean free path. Applied magnetic fields increase the plasma density and thus increase the deposition rate.

The low deposition rates also have certain advantages; for example, they do 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 coating morphology. Sputtered coatings grow in a complex plasma environment. The coating adherence, coherence, and morphology are directly affected by (1) sputter etched or biased surface, (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 basically 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 in both 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 these characteristics, relatively thin films in the 0.2 to 10 μm range can be used where previously thicker films were required. It can be implied, therefore, that the coating attachment to the surface is more important than the volume of coating present.

It is well known that stress induced peeling, which is caused by internal stresses in the film, increases with film thickness. Therefore, in sputtered films, which are usually very thin (<1 μm), the stress induced peeling effect is minimized.

A diverse range of coating morphologies and properties can be reliably produced by controlling the various sputtering parameters and the substrate conditions. The nucleation and growth of the sputtered film can be varied and this would in turn affect the film properties. Morphological changes (preferred texturing: columnar, equiaxed and even epitaxial growth) in the coating can be initiated. The grain size can be decreased substantially, and this reduction will increase 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 dull and matte appearance at bias potential. Since a detailed discussion of this subject is outside the scope of this paper, one is referred to Refs. 1 to 9.

SOME PRACTICAL USES OF SPUTTERING

The sputtering process is primarily used in sputter deposition technology. However, high rate sputtering techniques have been developed which can achieve sputtering rates up to 250 μm/hr. Thicknesses up to, but not limited to, 0.63 cm have been achieved. As a result, commercial interest has developed in thick deposits. Fabrication by sputtering of free standing shapes such as sheet, tubing, and inner and outer cylindrical structures with coolant passages for thrust chambers has been developed as illustrated in Fig. 5.

Sputter etching provides an alternate technique to chemical etching. The outstanding features are that it is universally applicable to all materials, it eliminates undercutting, and it is widely used for pattern delineation.

Of all the specific industrial areas the greatest sputtering activity is in microelectronics and microminituarization such as integrated thin film circuit technology. In the last 10 years sputtering has not only spread rapidly in the mechanical area but also in practically all areas which require films that are difficult or impossible to handle by other means. Just a few areas where sputtered coatings have an increasing impact are corrosion and high temperature oxidation protection, reduction of friction and wear, solid film lubrication, decorative purposes, replicating techniques, biomaterials for surgical implants, and solar cell development.

Several specific examples will illustrate how sputtered films function in these 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 [10, 11]. An endurance life evaluation is shown in Fig. 6 where sputtered MoS_2 films are compared to two other application techniques. The endurance lives of bearings sputter coated with a duplex coating (0.1 μm thick underlayer of Cr_3Si_2 and subsequently with 0.6 μm of MoS_2) were greatly improved over the lives of those bearings which had MoS_2 films directly applied as shown in Fig. 7. Teflon PTFE (polytetrafluoroethylene) has been successfully sputtered with excellent adherence on metal, glass, paper, and wood surfaces. Fig. 8 shows 0.1 μm thick PTFE films sputtered on hypodermic needles. Special formulations of modified silicon carbide and other refractory carbides have been sputtered on airborne components such as first-stage compressor blades. These components operate in severe environments and have to be protected from corrosion oxidation, errosion, and abrasion

[12]. An interesting approach is to sputter cattle bone on metallic prosthetic devices used as surgical implants for hip bone replacements. The sputtered bone film promotes bone growth and attachment to living bone [13].

SUMMARY OF RESULTS

The sputtering process is primarily used in thin-film deposition technology. Because higher sputtering rates have been attained, sputtering is now used for fabricating intricate mechanical components (tubing, cylinders with passages, etc.). Finally, the sputtering process is being used as a universal nonchemical etching technique.

In coatings technology sputtering has yet unexplored potentials due to the fact that almost any material can be sputtered in proportions and relations that are not regulated by classic thermodynamics and phase interrelationships. Many sputtering modes and configurations can be used to achieve chemical compositions which range from stoichiometric to nonstoichiometric. Coatings with gradual changes in composition and laminated and dispersion strengthened structures can also be obtained using these configurations.

The unique sputtering features of versatility, momentum transfer, stoichiometry, sputter etching, target geometry, precise controls, flexibility, and sputtering rates contribute to the outcome of the desired coating.

The sputtered films generally exhibit strong adherence and coherence, and the coating morphology can be controlled by the sputtering parameters. As a result, thin sputtered films having 0.2 μm thicknesses are sufficient for many applications. Sputtered MoS_2 lubricant films 0.2 μm thick exhibit superior performance during sliding friction, and sputtered Teflon (PTFE) and sputtered cattle bone have found new useful applications.

REFERENCES

1. Wehner, G. K., and Anderson, G. S., Handbook of Thin Film Technology, Chap. 3, L. I. Maissel and R. Glang, eds., McGraw Hill, 1970, pp. 3-1 to 3-38.

2. Miassel, L., Handbook of Thin Film Technology, Chap. 4, L. I. Maissel and R. Glang, eds., McGraw Hill, 1970, pp. 4-1 to 4-44.

3. Carter, G., and Colligow, N. S., Ion Bombardment of Solids, Chap. 7, Heinemann Educational, London, 1968, pp. 310-353.

4. Mattox, D. M., Sputter Deposition and Ion Plating. American Vacuum Society, 1973.

5. Brown, S. C., Introduction to Electrical Discharges in Gases, John Wiley and Sons Inc., 1966.

6. Vossen, J. L. and O'Neill, J. J., RCA Review, Vol. 29, pp. 149-173, 1968.

7. Chopra, K. L., Thin Film Phenomena, McGraw-Hill, 1969.

8. Thornton, J. A., Journal of Vacuum Science and Technology, Vol. 11, No. 4, pp. 666-670, 1974.

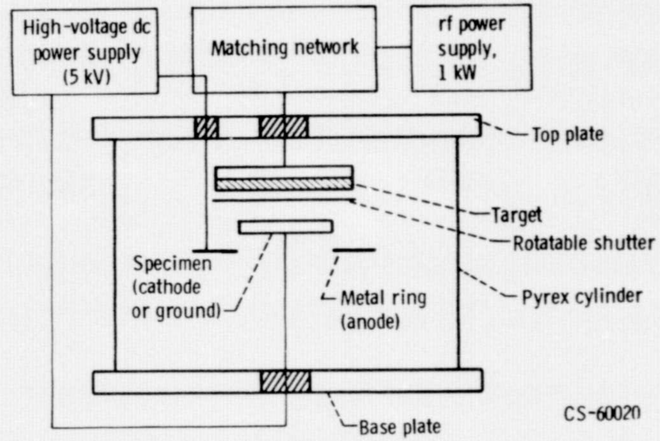
9. Notis, M., High Frequency Heating Review, Vol. II, No. 8, Lepel High Frequency Laboratories, Inc., pp. 4-6.

10. Spalvins, T., "Sputtering - A Vacuumed Deposition Method for Coating Material," Paper No. 72-DE-37, presented at the Design Engineering Conference and Show of the ASME, May 8-11, 1972.

11. Spalvins, T., ASLE Proceedings - International Conference on Solid Lubrication, American Society of Lubrication Engineers, 1971, pp. 360-370.

12. Gentner, K., "Potential of Sputtered Films as Protective Coatings," NADC-75038-30, Naval Air Development Center, 1975 (N76-17251).

13. Shaw, B. J. and Miller, R. P., "Sputtering of Bone on Prosthesis," Patent 3,918,100, United States, Nov. 1975.



(a) Schematic diagram.

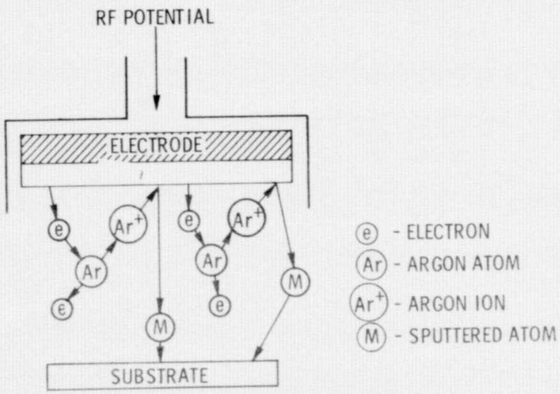
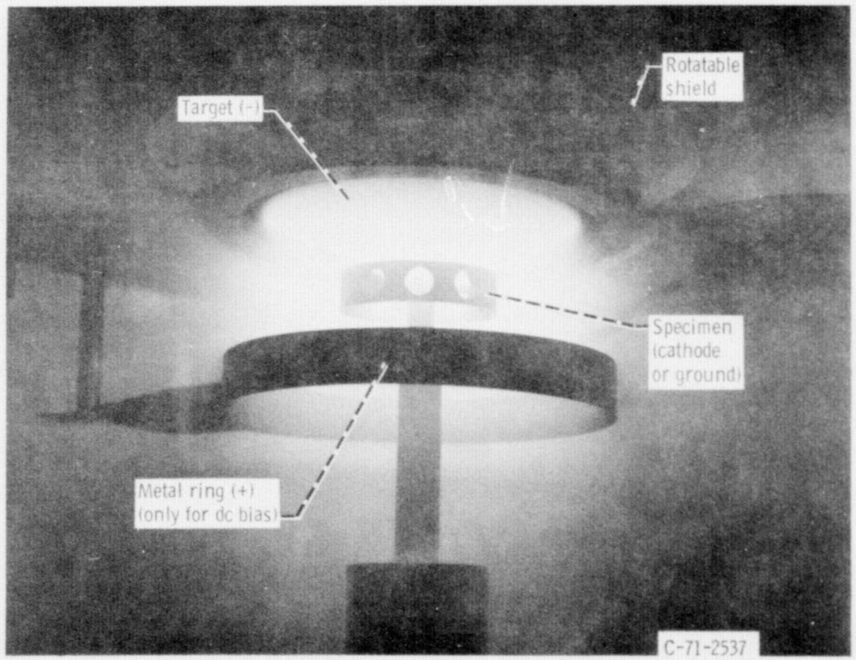


Figure 1. - Schematic of sputtering process.



(b) View of apparatus during sputter coating.

Figure 2. - Radiofrequency diode sputtering apparatus with direct-current bias.

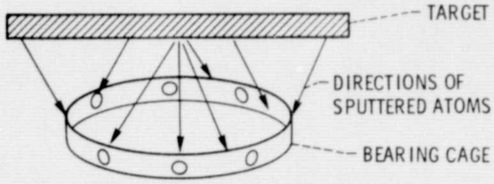


Figure 3. - Schematic of sputter coating complex surfaces.

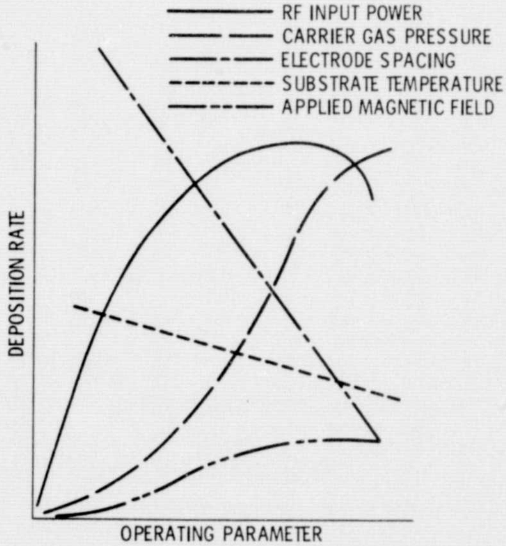


Figure 4. - Deposition rate as a function of various operating parameters.

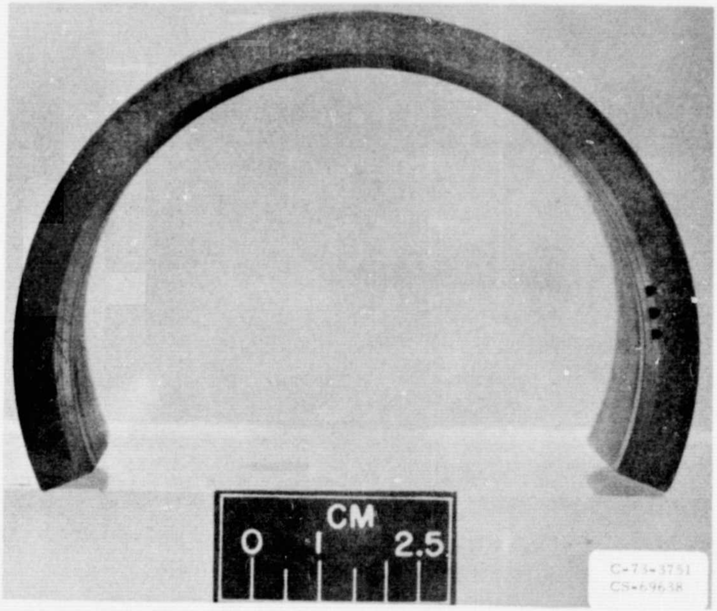


Figure 5. - Fabrication of cylinders by sputtering.

E-8944

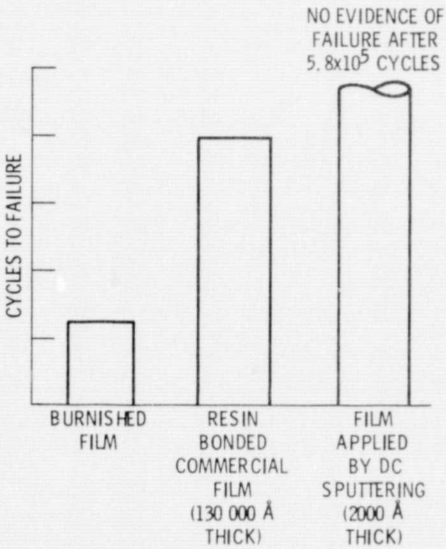


Figure 6. - Endurance lives of MoS_2 films applied by various techniques.

ORIGINAL PAGE IS
OF POOR QUALITY

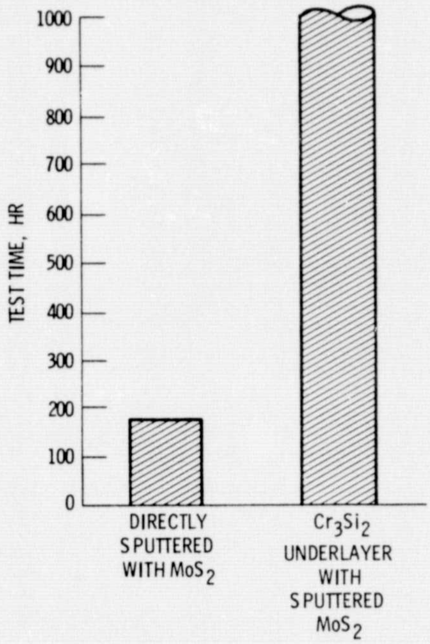


Figure 7. - Endurance lives of 440C stainless-steel ball bearings with sputtered MoS_2 films on races and cage - with and without a Cr_3Si_2 underlayer.

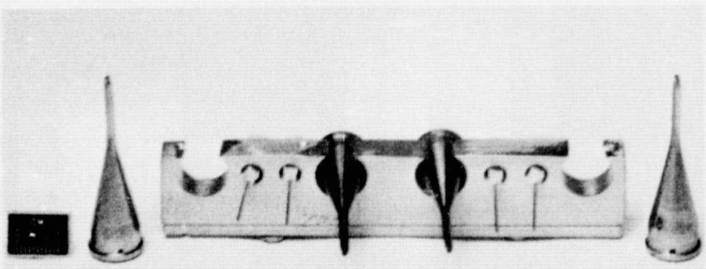


Figure 8. - Hypodermic needles and protective housings with sputtered teflon.