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Plasma Deposition and Surface Modifcation Techniques for Wear Resistance

T. Spalvins
Lewis Research Center
Cleveland, Ohio

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ABSTRACT

The ion-assisted or plasma coating technology is discussed as it applies to the deposition of hard, wear resistant refractory compound films. Of the many sputtering and ion plating modes and configurations the reactive magnetron sputtering and the reactive triode ion plating techniques are the preferred ones to deposit wear resistant coatings for tribological applications. Both of these techniques incorporate additional means to enhance the ionization efficiency and chemical reaction to precision tailor desirable tribological characteristics. Interrelationships between film formation, structure, and tribological properties are strictly controlled by the deposition parameters and the substrate condition. The enhanced ionization contributes to the excellent adherence and coherence, reduced internal stresses and improved structural growth to form dense, cohesive, equiaxed grain structure for improved wear resistance and control.

INTRODUCTION

To maximize wear resistance for functional mechanical components, various chemical processes and coating techniques have been used to obtain a hard surface layer or coating. Basically, hardened surfaces improve abrasive wear resistance by increasing surface hardness and improving adhesive wear resistance through the reduction of the real area of contact and by reducing the chemical affinity between the materials at the rubbing interfaces. In the last two decades, the plasma or ion assisted vacuum deposition techniques and surface treatment processes have emerged to supplement the well-known case hardening, flame spraying, electroplating, physical vapor deposition (PVD), and chemical vapor deposition (CVD) techniques.

Plasmas are a convenient source of energetic electrons, ions, and activated energetic evaporants which can be used in a variety of surface treatment processes. On the basis of how the glow discharges are excited and applied to surfaces two distinct types of surface hardening technologies can be distinguished: (1) the deposition of distinct overlay refractory compound coatings by sputtering and ion plating and (2) the surface property modification on the base materials without forming a discrete coating by ion implantation and ion nitriding.

In this review particular attention is directed to the emerging plasma deposition techniques (sputtering and ion plating). These techniques are restricted to processes where particle condensation on the substrate is initiated under the direct action of either ion flows or energetic neutrals produced by charge exchange. The recent interest and activity in these techniques originates from the fact that any refractory compound coating in any desired chemical composition can be synthesized and deposited with a preferred morphological structure. The increased energizing of the deposition process generally leads to improved film adherence, favorable morphological growth, higher density and reduced residual stresses in the film. In addition these coatings are generally thin enough (< 10 μm) so that for all practical purposes the finished dimensions are unchanged by the coating process, and the surfaces coated are not subjected to high temperatures.

Over the past several years rapid advances have been made in the sputtering and ion plating equipment design with the object being to increase

the ionization efficiency of the evaporant flux. Ionization can be generally enhanced either by increasing the electron path within the discharge in magnetron sputtering or by providing additional ionization sources such as a thermionic emitter or a positive electrode having a triode ion plating arrangement.

The enhanced ionization affects the nucleation and growth sequence which in turn favorably affects the crystallographic structure and the morphological growth. The columnar structure which is characteristic of most coating techniques causes mechanical weakness due to the high porosity and internal stresses. The enhanced ionization has the tendency to form a more equiaxed structure with a smaller grain size and higher density which contributes to an increased cohesive strength.

With the enhanced ionization the activation energy is also increased and this is utilized to promote chemical reactions when reactive gases such as N_2, C_2H_2, etc. are introduced to form the respective nitrides and carbides. In the reactive mode of sputtering and ion plating, concurrent synthesis and deposition can be performed with a wide composition range to generate the optimum properties for wear resistance.

In the deposition of carbides, nitrides, silicides, borides, and oxides the reactive magnetron sputtering and the reactive (triode) ion plating techniques are the preferred ones to optimize the tribological characteristics. Of the refractory compounds TiN and TiC are most widely used and investigated. However, a wide range of refractory compound coatings such as SiC, Si_3N_4, HfNi, Cr_2B, Mo_2C, Cr_3C_2, $MoSi_2$. TaC, BN, etc. have been plasma deposited for wear resistance purposes. The TiN and TiC wear resistant coatings are extensively used in metal working and forming operations to improve the working surfaces of cutting and forming tools. Particular emphasis is placed, for example, on the coating of cemented carbide inserts, stamping and punching dies, thread guides, etc. The plasma deposited coatings have the advantage that they can be applied as a final processing step. It does not require post processing of grinding and lapping to restore component dimensions and surface finish. Temperature-sensitive bulk materials such as tool steels can now be directly coated with carbides and nitrides. The objective of this review is to describe the trends in sputtering and ion plating technology as it applies to the deposition of refractory compound films in order to confer precision tailored wear resistant characteristics.

GLOW DISCHARGE CONSIDERATIONS

Glow discharge or plasma can be generated by an electrical discharge or by radio frequency. The working pressure is determined by the method of plasma generation and the range is usually between 1 to 20 mTorr. Plasmas which are produced under normal laboratory conditions such as in sputtering and ion plating have a low degree of ionization, less than 0.1 percent. Over the past years rapid advances have been made in equipment design to incorporate additional ionization sources in order to increase the efficiency.

During the ion plating, for instance, there are two phenomena in the glow discharge which have not been fully resolved, in spite of the numerous experimental and theoretical investigations. The ionization efficiency (the percentage of evaporant atoms which are ionized), and the energies of the evaporant

flux. When the atoms of the film material are injected into the glow discharge, a small portion will be ionized primarily by electron atom collisions or by metastable atom collisions (Penning ionization) (ref. 1).

The plasma can be used for sputtering and also to promote chemical reactions. Glow discharges excited in inert and active gases and their mixtures are primarily used in the synthesis and deposition of refractory compound coatings. Gas discharges that incorporate chemical reactions comprise a reaction volume of great complexity which consists of a melange of molecules, atoms, atomic ions in various stages of excitation, electrons, photons, etc. It should be noted, that the understanding of the microstructure of the films deposited has progressed further than that of the compositional makeup of the glow discharge from which the films are formed.

A complete mechanistic description of film formation requires knowledge of such items as (1) electron impact and ionization rates of the reactants, (2) surface recombination rates, (3) ion molecule rates of species produced in a discharge, (4) neutral-neutral reaction rates and their temperature dependence in the discharge and on the surface (ref. 2).

THE SPUTTERING PROCESS

Sputtering technology offers a great versatility and flexibility in refractory coating preparation, since the sputtered coatings can be tailored in any preferred chemical composition, and the coating morphologies can be modified. The sputtered particles are generated by impact and are transferred by a momentum transfer process. Therefore, it can be considered a "cold process" and has been widely described as such (refs. 3 to 5).

Numerous sputtering modes and configurations are available based on such considerations as the type of potential applied (dc or rf), utilization of multiple targets, type of gas used (inert or reactive), auxiliary electrodes, magnet utilization - magnetron sputtering, etc., which all contribute to the extreme flexibility in coating preparation.

The two sputtering modes which have emerged in the deposition of the refractory compound coatings for wear resistance are reactive rf and reactive magnetron sputtering. Since magnetron sputtering incorporates more efficient plasma discharges, it offers relatively high deposition rates (0.1 μm/min) at low substrate temperatures, thus permitting coating of thermally sensitive materials.

The sputtering targets can be either manufactured from the refractory compounds such as TiC or TiN or made from the pure elemental refractory metal Ti. Regardless of the particular target selection the reacitve mode must be used. When, for instance, the TiN or TiC target is used an active gas such as N_2 or C_2H_2 must be added to the system and carefully controlled, to maintain the stoichiometry, otherwise the films are deficient in the gaseous deposited component.

Reactive Radio Frequency (rf) Sputtering

In rf sputtering the target is energized by the application of rf (13.56 MHz) power and the basic configuration is schematically and photographically

shown in Fig. 1. The rf current through the target injects power into the inert gas, thus generating the ion plasma rf fields. Further, the rf field generated in the glow discharge, prevents charge accumulation and as a result insulating materials and dielectrics can be sputtered (refs. 3 and 4).

The targets used generally have a planar configuration and are fabricated of the refractory compound materials such as TiC, TiN, HfN, Si_3N_4, etc. The specimen may be maintained at ground or biased negatively. The specimen is first sputter cleaned by applying a 2- to 5-kV negative potential with respect to the ring and establishing a glow discharge as in dc sputtering. Following the dc sputter etching the specimen is energized by the application of rf power. During the rf sputtering process, the dc voltage impressed on the substrate can be varied or turned off. When the refractory compounds such as carbides and nitrides are sputter deposited, the appropriate reactive gas such as N_2 or C_2H_2 is introduced into the system. The flow rate is carefully controlled to maintain the corresponding stoichiometry or synthesize the desirable chemical changes in the coating (refs. 5 to 11).

Reactive Magnetron Sputtering

To generate more effective plasmas permanent magnets are placed behind the flat target as shown in Fig. 2. Magnetic fields of a few hundred gauss are applied at right angles to the electric field. The magnetic lines of force exit and reenter the cathode, forcing electrons into spiral motions along the field lines forming a closed loop where the electrons are trapped. As a result, the probability of collisions between the electrons and argon gas atoms is greatly enhanced and ionization efficiency is increased. However, it should be pointed out that the magnetic field affects and directs the electrons but not the ions. At the same time the specimen is just exposed fractionally to the secondary electron bombardment, which significantly reduces the substrate heating. Consequently the increased ionization has beneficial effects in terms of increased sputtering rates, increased activation for chemical reaction in the reactive mode and reduced substrate temperature. Because of these distinct advantages, magnetron sputtering is the preferred technique for reactively depositing carbides and nitrides (refs. 12 to 14).

Further, TiN films display different attractive gold-like colors, when Ti is sputtered in a N_2-Ar gas mixture as the partial pressure of N_2 is varied. The color is important for decorative applications and also protects the surface against wear. The color can also be used as an indication of such film characteristics as hardness, resistance to wear, and corrosion.

It has been reported (ref. 15) that the N_2 flow rate above a certain critical level results in a darkened film without exhibiting the pleasing gold-like appearance. These darkened films have lower hardness and less resistance to abrasion and corrosion.

ION PLATING PROCESS

Ion plating combines in principle the high throwing power of electroplating, the high deposition rates of thermal evaporation, and the high energy impingment of ions and energetic atoms of the sputtering process. The basic difference between sputtering and ion plating is that the sputtered material is generated by impact evaporation and transfer occurs by a momentum transfer

process, whereas in ion plating it is by thermal evaporation. The ion plating process is more energetic than sputtering, since the process uses a high substrate bias of several thousand volts to directly accelerate the positively ionized evaporant atoms into the substrate (refs. 12 to 16). The basic ion plating system consists of a dc-diode configuration, where the specimen is made the cathode of the high voltage dc circuit with an evaporation source as shown in Fig. 3.

The interest in ion plating originates from its three unique features. The high energy flux of ions and energetic neutrals contribute to the excellent adherence of film to substrate, desirable microstructural growth of the film and when used in the reactive mode provides activation energy to synthesize stoichiometrically uniform compound films. The high throwing power provides for three-dimensional coverage, which results in high deposition rates.

With typical ion plating conditions (where the voltage is 3 to 5 kV, argon pressure is 20 mTorr and cathode current density is 0.3 to 0.6 mA/cm^2) the ionization is relatively low, less than 1 percent. It has been estimated that under these conditions the ions carry only 10 percent of the energy dissipated while the energetic neutrals carry 90 percent (ref. 16). Thus the plating flux consists of a small number of ions and a large number of energetic neutrals. The ions and the neutrals may have a distribution of energies from thermal 0.2 eV up to the voltage applied to the discharge. Estimates indicate that the average energies of the ions and the neutrals are of the order of 100 eV (ref. 16).

The reactive mode of ion plating shows distinct advantages in the deposition of the nitrides and carbides. In this mode it still offers excellent adherence due to the formation of a graded interface. Also the nitrides and carbides such as TiN, TiC can be stoichiometrically synthesized and uniformly reproduced (refs. 17 to 23). It is important to understand that from a tribological point of view the excellent adherence is not the only controlling factor for optimum wear resistance. The microstructure and morphological growth of the coating is of equal importance. The conventional ion plating does improve the grain structure, however, the structure still tends to be columnar. The objective is to increase the ionization efficiency which has the tendency to affect the nucleation and growth sequence to produce fine equiaxed structures of high density at lower temperatures.

A number of improvements have been investigated to increase the ionization efficiency. Schematic diagrams for such improvements are shown in Fig. 4. The multicathode technique (ref. 24) aims to increase ionization with the emission of thermal electrons from hot tungsten filaments placed in the evaporation area. The high frequency technique (rf ion plating)(refs. 25 to 26) utilizes an rf coil which is connected to a 13.56 MHz (1 kW) generator through a matching box to promote ionization by a high frequency magnetic field. Use of an induction heated evaporation source (ref. 27) where there is a high frequency magnetic field generated by electron trapping increases the ionization. The incorporation of a positive electrode known as a positive discharge probe (ref. 28), or a low-voltage high-current electron gun with a hot hollow cathode discharge gun (HCD) as an evaporation source (refs. 29 and 30) will also increase ionization. A combination of a thermionic emitter and a positive probe (ref. 21) will do likewise. A special type of ion plating is the deposition with ion clusters (cluster ion plating) where a special evaporator produces ionized vapor clusters which create an effect equivalent to a state of in-

creased ionization. The aforementioned techniques generally increase the ionization ratio by a factor of 10 and are used mainly for the deposition of hard wear resistant coatings.

ION BOMBARDMENT EFFECTS ON COATING CHARACTERISTICS

During sputtering or ion plating, ions transfer energy, momentum and charge to the substrate and the growing films. Even without acceleration the ionized species greatly influence the critical parameters of the condensation and nucleation process for film formation. An interrelationship exists between the film formation characteristics, structure, chemical composition and the wear resistant properties which are strictly controlled by the deposition parameters and the substrate condition. The basic objectives in the deposition of refractory compound films are: strong adherence and coherence, low internal stresses and change from the columnar structure to a more dense, isotropic equiaxed structure.

Adherence

The hard, wear resistant refractory compound coatings are usually associated with poor adherence to the substrate. All interfaces represent a break in the normally uniform crystallinity and/or composition. This abrupt change or mismatch is reflected in the hardness, coefficient of thermal expansion, and thermal conductivity. This discontinuity may be reduced or eliminated by inducing a gradual transition from the interface to the outer surface of the coating. A hardness gradient for instance can be produced either by reactive sputtering or reactive ion plating by varying the composition of the reactive gas as shown in Fig. 5 for TiN (ref. 31). In ion plating the deposition can be performed at a constant pressure due to the formation of a graded-fused interface. The graded interface and consequently the strong adherence is generally attributed to the sputter etched surface and the high energy evaporant flux. The exact reaction mechanism for the formation of such an interface is not fully understood, but the controlling factors are sputter etched surface, diffusion, implantation, atomic mixing, nucleation and growth as shown in Fig. 6. These factors can act separately or in various combinations depending on the film/substrate compatibility. Because of the exceptional adherence, the reactive ion plating is widely investigated in the deposition of nitride and carbide coatings.

Structure

The structure of deposited coating can be improved by increasing the substrate temperature. For instance the chemical vapor deposition (CVD) techniques are industrially used to deposit TiN and TiC coatings on cemented carbide cutting tools to improve their cutting performance The drawback of the CVD technique is the high temperature which is required for optimizing the adherence and structural integrity. Temperature sensitive materials such as alloy tool steels used as cutters, drills, etc. cannot be directly CVD coated with TiN or TiC because the processing temperature which is usually above 900° C is above the tempering temperature of the steel. Under these conditions the substrate material is exposed to dimensional and phase changes and a reduction in hardness.

It is well recognized that films prepared by sputtering show a wide range of microstructures as the substrated temperatures increase. This has led to

the development of the structure zone model (SZM) shown in Fig. 7 (ref. 32). The model consists of the formation of four zones which depend on the ratio of the surface temperature (T) to the melting point of the deposited material (T_m). The structural T/T_m dependence is affected by the surface diffusion processes and the bulk processes that characterize recovery and recrystallization (ref. 32). The coatings in zone 1 have tapered columnar crystals separated by open, voided longitudinal boundaries. This structure is generally too porous to support applied stresses as required in tribological processes. Coating in zone T (transition) region consist of densely packed fibrous grains, where in zone 2 the structure has columnar grains separated by distinct, intercrystalline boundaries. Finally, in zone 3 bulk diffusion has predominant influence on the final structure of the coating and it consists of equiaxed, dense, recrystallized grains.

Recovery and/or recrystallization reduces the internal stresses, and this type of structure is the preferred one for the deposition of wear resistant high melting refractory compound coatings. However, the high T/T_m which is required for carbide and nitride deposition unfavorably affects the substrate materials such as tool steels. This high temperature limitation can be overcome by intensifying the glow discharge, for example, by increasing the specimen to substrate current density and this has the same effect as raising T/T_m directly. It will also lead to the development of a structure characteristic of the higher zone.

To maximize the specimen ion current, additional ionization sources such as positive electrodes or thermionic emitters are incorporated in the ion plating system to provide a triode configuration. These additional electrodes are used to intensify the discharge and they also allow for the varying of discharge current independently from the bias voltage on the specimen. The high energy evaporation flux produced offers means of obtaining dense, fine grained, equiaxed microstructures representative of a higher T/T_m. This approach had been primarily investigated and developed for the deposition of carbides and nitrides. The additional energy applied to the condensate increases the bombardment effects during the deposition, which favorably influences the nucleation and growth characteristics. It has been reported that energy (>500 eV) ion bombardment can suppress the formation of a distinct columnar structure (ref. 33). The high rate of nucleation tends to form a uniform, fine grained, high packing density, smooth film, which contributes to an increased cohesive strength. This increased cohesive strength improves the film's integrity, therefore the likelihood of a breakup of the coating during the wear is significantly reduced.

Internal Stresses and Film Thickness

The hard wear resistant refractory compound films are generally in a high state of stress. The total internal stress is composed of the thermal stress σ_t and intrinsic stress σ_i

$$\sigma_{tot} = \sigma_t + \sigma_i$$

The thermal stress is due to the differences in the thermal expansion coefficient of the coating and the substrate material. This difference is very pronounced between the refractory compound coatings and the metallic substrate. Intrinsic stress is due to the accumulating effects of crystallographic defects of flaws formed in the coating during deposition.

Typical deposition conditions normally involve relatively low temperatures. At low T/T_m the intrinsic stresses dominate over thermal stresses as shown in an idealized representation in Fig. 8 (ref. 34). Thus, the poor adhesion for the high melting point materials (carbides and nitrides) can be attributed to the intrinsic stresses. In addition to the temperature effects (T/T_m), which affect the internal stress values, the degree of ion bombardment also strongly influences the internal stresses. With increasing ion flux, the stress changes from tensile to compressive in nature. Typically evaporated films retain high tensile stresses while sputtered films may have tensile or compressive stresses depending on the nature of energetic ion and neutral bombardment. Ion plating which has the highest energy flux generates a graded-fused interface where the compressive stresses are distributed and appreciably reduced.

The film stresses also vary with film thickness, as a critical thickness is exceeded, poor adherence is caused by cracking or buckling. Whenever the shear stress exceeds the yield stress at the interface, or within the film itself, separation will occur. A typical film delamination within a sputtered Cr_3C_2 film about 3.5 μm thick is shown in Fig. 9.

Substrate Topography

In addition to the process parameters the surface topography of the substrate and the resultant coating has a pronounced effect on the wear behavior. It is impossible to prepare surfaces that are atomically smooth over extended areas. Microdefects, however, can be eliminated. Microdefects such as dislocations and point and extended defects limit the obtaining of a smooth surface. Various unusual crystallographic defect growth structures are observed in the matrices of sputtered and ion plated carbide, nitride, and silicide films. Typical SEM micrographs in Fig. 10 show the surface views of sputtered Cr_3C_2 films with defect growth features. Substrate irregularities or imperfections are the preferential nucleation and growth sites of these defects. At these nucleation sites accelerated growth occurs relative to the matrix growth, and as a consequence the crystallographic defects extend above the matrix surface. These surface defect structures are stress raisers and weaken the film structure by fracturing and also are potential sources for producing damaging abrasive wear particles. These crystallographic defect structures have the greatest damaging effects on the hard wear resistant coatings.

CONCLUSIONS

The importance of ion-assisted coating technology (sputtering and ion plating) has increased for the deposition of hard refractory compound coatings in tribology to reduce friction and wear. Particularly the TiC and TiN coatings are extensively used and investigated in the metal working and forming operations to improve the working surfaces of cutting and forming tools.

At the fundamental level the plasma deposition environment is extremely complex and insufficient information exists concerning ionization efficiency, kinetic energy, and the total compositional makeup of the plasma. For tribological applications preferably reactive magnetron sputtering and triode ion plating are used. Both of these techniques incorporate additional means to enhance the ionization efficiency and chemical reaction and are used to pre-

cision tailor desirable tribological characteristics. The enhanced ionization in both techniques contribute to the excellent adherence and coherence, reduced internal stress, improved structural growth to form dense, cohesive, equiaxed grain structure all of which have a tendency to improve wear resistance and control the tribological performance. The disadvantage of these coatings lies mainly in their newness. Further, the best coating compositions and the optimum processing parameters have yet to be established.

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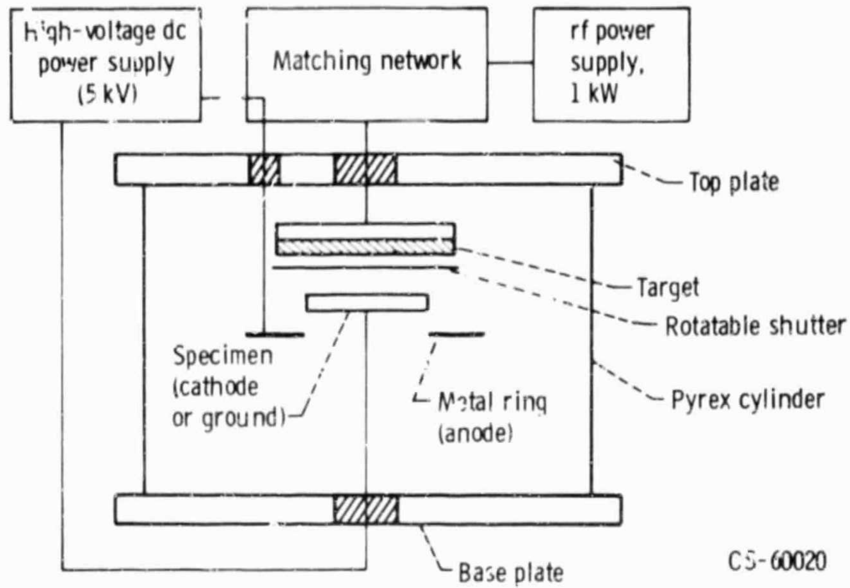
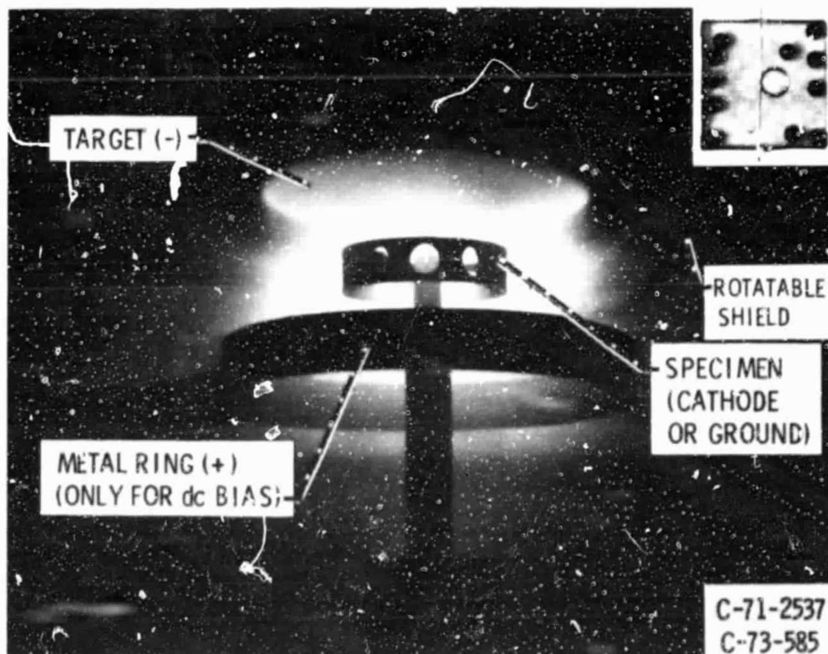


(a) Schematic diagram.



(b) View of apparatus during sputter coating.

Figure 1. - Radiofrequency diode sputtering apparatus with direct-current bias.

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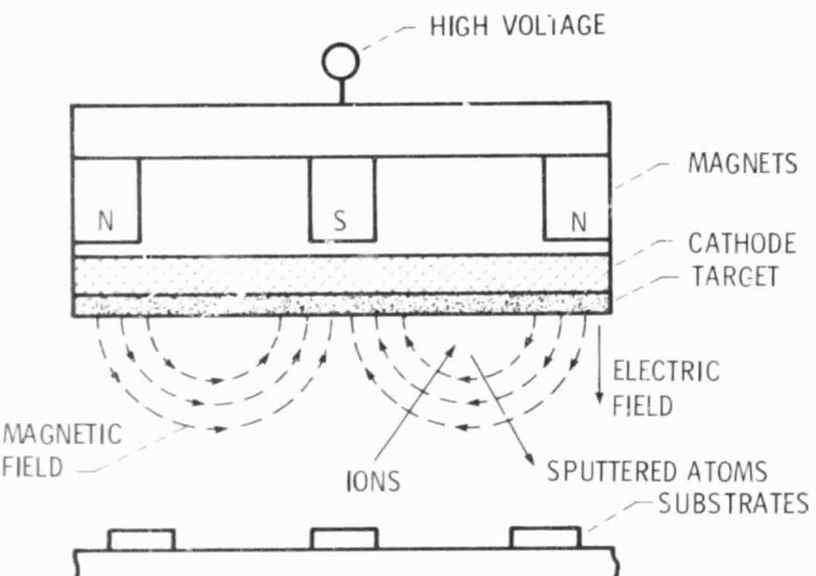
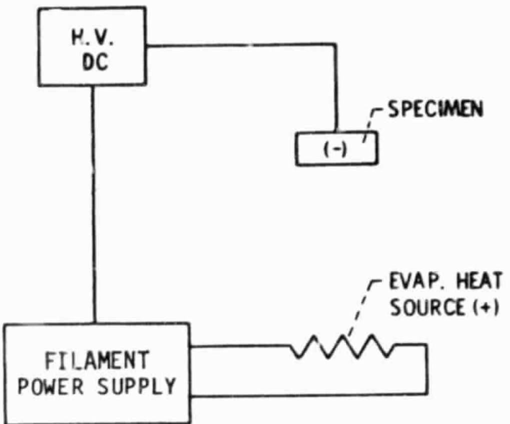
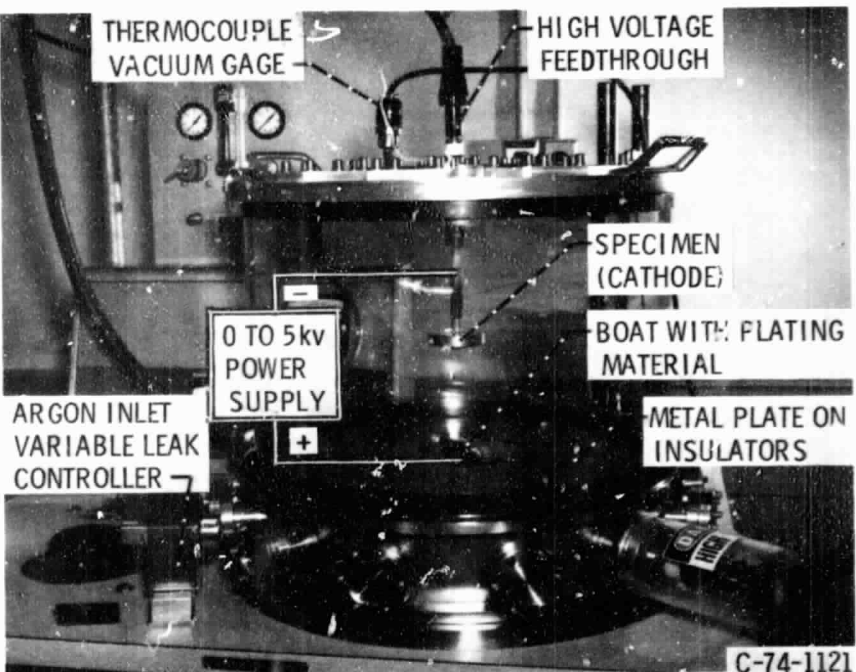


Figure 2. - Magnetron sputtering concepts.



(a) SCHEMATIC.



(b) ION PLATING CHAMBER.

Figure - Ion plating system.

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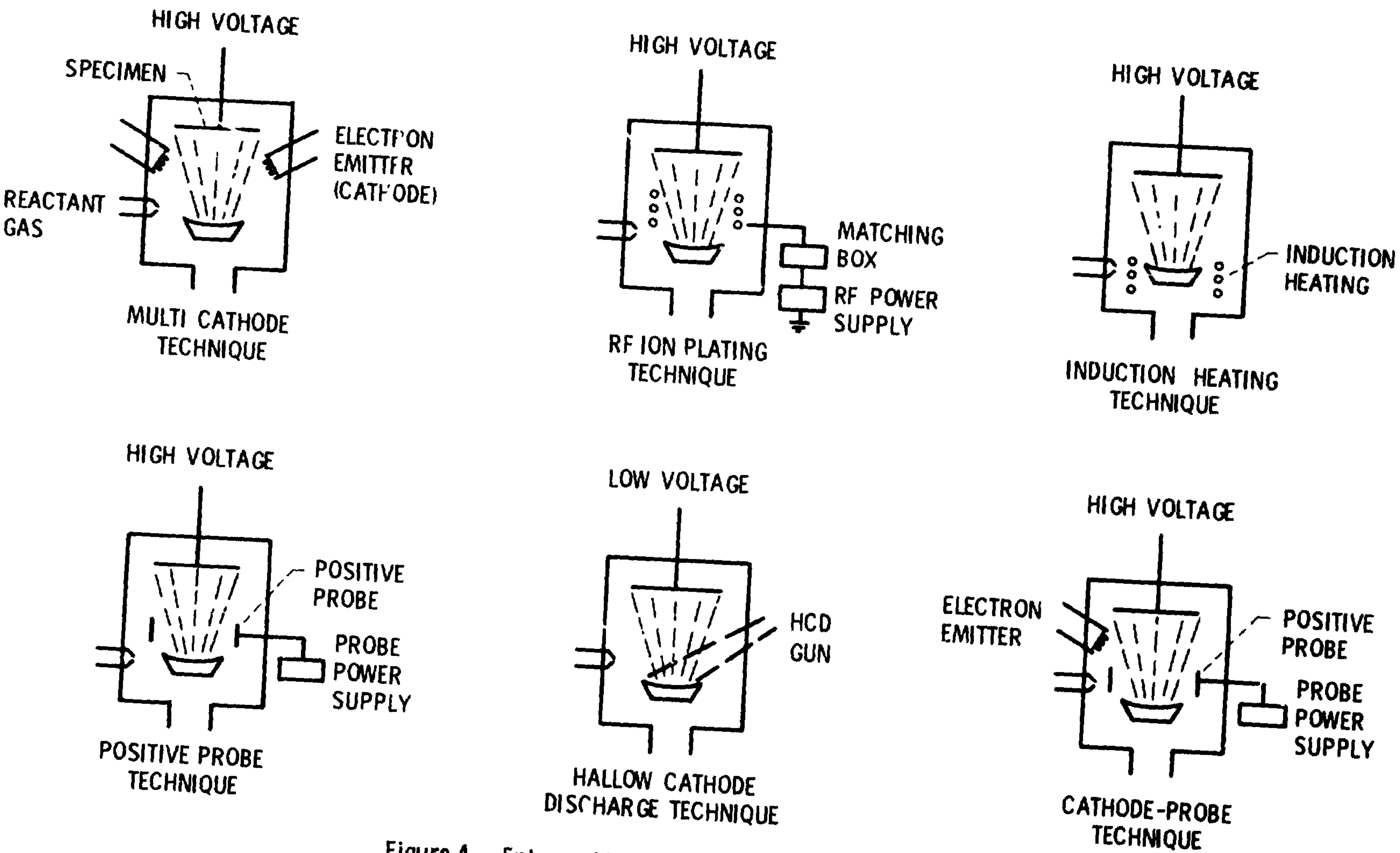

Figure 4. - Enhanced ionization techniques of ion plating.

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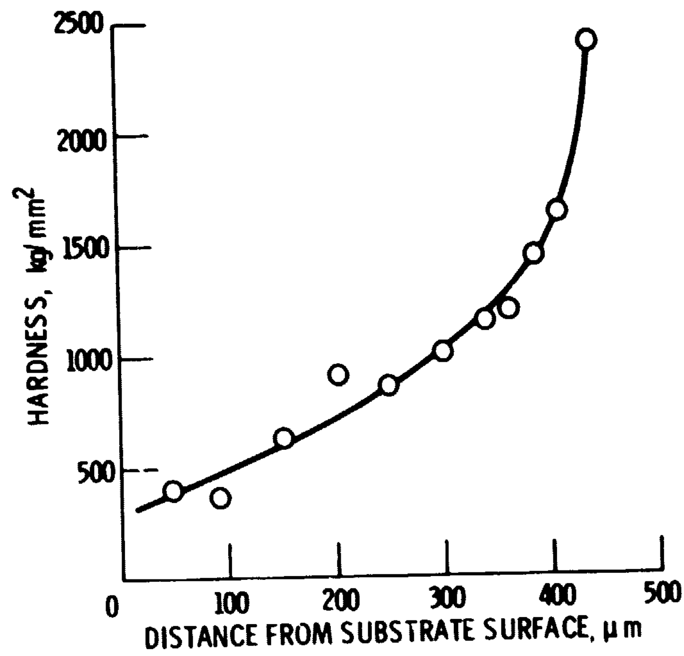

Figure 5. - Hardness gradient of TiN coating produced by reactive ion plating (ref. 31).

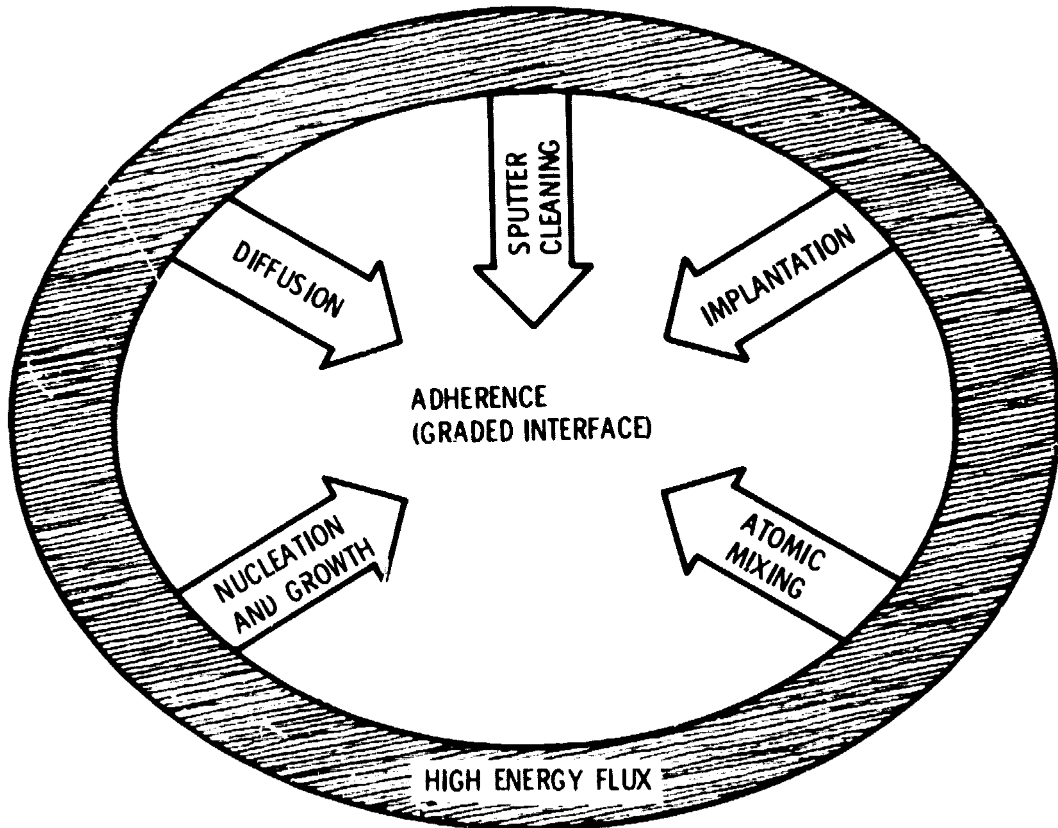

Figure 6. - Illustration of the factors which influence adherence and interface formation during ion plating.

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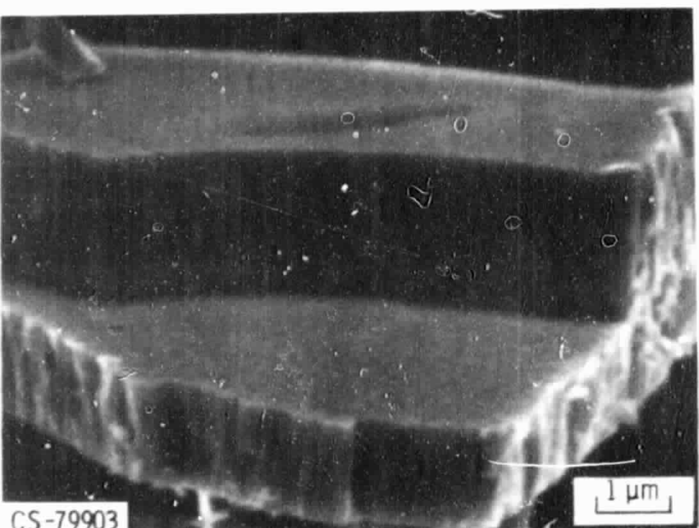
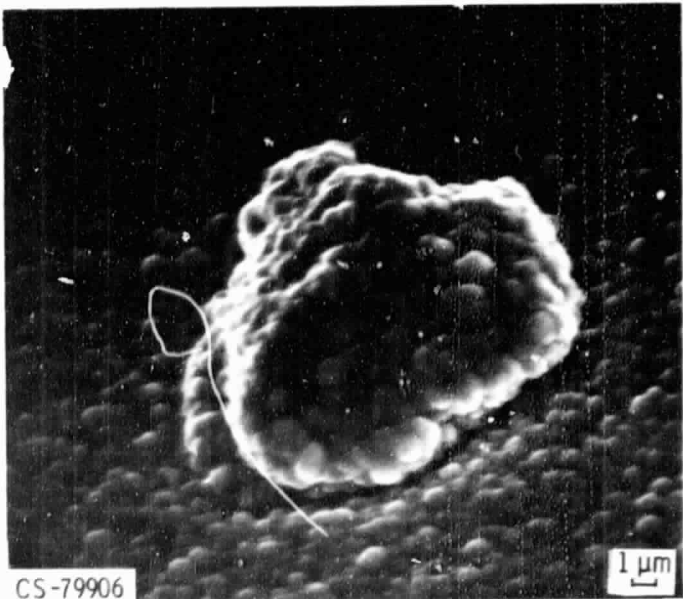


Figure 9. - Separation within a 3.5 μm film of sputtered Cr_3C_2.



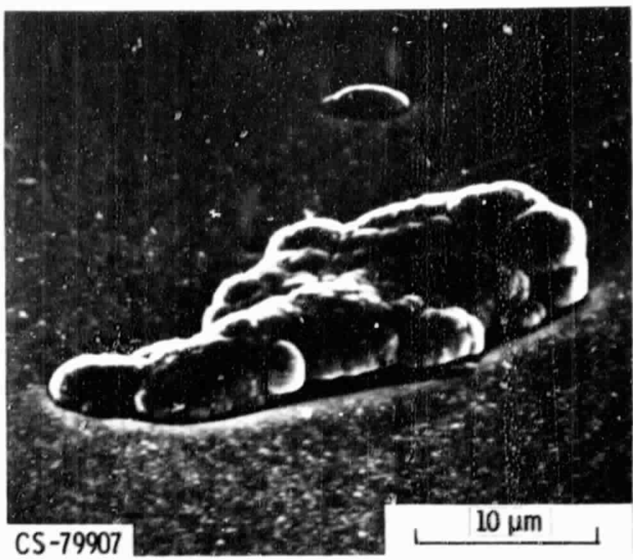


Figure 10. - Surface defects in sputtered Cr_3C_2 film.