

NASA Technical Memorandum 88885

(NASA-TM-88885) PLASMA ASSISTED SURFACE  
COATING/MODIFICATION PROCESSES: AN EMERGING  
TECHNOLOGY (NASA) 15 p CSCL 13H

N87-12708

Unclassified  
G3/31 44619

# Plasma Assisted Surface Coating/Modification Processes: An Emerging Technology

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Prepared for the  
First International Ion Nitriding Conference  
cosponsored by the American Society for Metals  
and NASA Lewis Research Center  
Cleveland, Ohio, September 15-17, 1986

NASA

PLASMA ASSISTED SURFACE COATING/MODIFICATION  
PROCESSES: AN EMERGING TECHNOLOGY

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ABSTRACT

The purpose of this paper is to introduce and provide a broad understanding of the numerous ion or plasma assisted surface coating/modification processes. One should be aware of the principles of these processes before discussing in detail the ion nitriding technology. On the basis of surface modifications arising from ion or plasma energizing and interactions, it can be broadly classified as deposition of distinct overlay coatings (sputtering - dc, RF, magnetron, reactive; ion plating-diode, triode) and surface property modification without forming a discrete coating (ion implantation, ion beam mixing, laser beam irradiation, ion nitriding, ion carburizing, plasma oxidation). These techniques offer a great flexibility and are capable in tailoring desirable chemical and structural surface properties independent of the bulk properties.

THE PURPOSE OF THIS PAPER is to present an overview and focus on some of the most commonly used plasma assisted surface coating/modification processes in surface technology. Protection of material surfaces from hostile environments and severe operating conditions is of great technical and economic necessity, since surface-subsurface properties of materials determine the performance. Surface protection is required to minimize such effects as friction, wear, erosion, corrosion, high temperature oxidation and fatigue. The plasma assisted surface modification techniques offer a great flexibility and are capable in tailoring desirable chemical and structural surface properties independent of the bulk properties.

On the basis of surface modifications arising from plasma energizing and interactions, the plasma deposition/modification techniques can be broadly classified as deposition of distinct overlay coatings: sputtering (dc, RF, magnetron, reactive) (Refs. 1 to 8); ion plating (diode, triode, reactive) (Refs. 9 to 12); and surface property modification without forming a discrete coating: the ion beam techniques (ion implantation, ion beam mixing, laser beam processing) (Refs. 13 to 19) and the plasma thermochemical processes (ion nitriding, ion carburizing, plasma oxidation) (Refs. 20 to 23). The two distinct surface modifications resulting from these techniques are schematically shown in Fig. 1.

GLOW DISCHARGE CONSIDERATIONS

Plasmas used for surface modification are generally low pressure and temperature gas discharges sustained at  $10^{-3}$  to 10 Torr and are characterized by a small degree of ionization less than 0.01 percent. These plasmas are primarily produced by electron impact excitation, ionization and dissociation. Average energies range from about 1 to 10 eV, while the energies of ions and neutrals in the plasma are considerably less (about 0.1 eV). Consequently the plasma is at low temperature, essentially "cold," even though the electron energies can achieve temperatures on the order of  $10^4$  to  $10^5$  K.

Several types of discharges can be established, depending on the relationship between voltage and current as shown in Fig. 2. The abnormal glow in which the current increases with the voltage is used for the plasma assisted deposition techniques. As the voltage is raised the glow discharge/arc discharge transition threshold point is approached, and upon reaching this critical voltage the glow discharge collapses and high

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current density arcs form. Therefore it is essential to minimize cathode voltages if arcing is to be avoided.

During any surface processing the plasma activation energy promotes a physical effect, no matter what gas is used, it is always present, and a chemical effect present only when reactive gases are used. The physical aspects of the glow discharge have profound effects on the nucleation and growth kinetics of the deposited films.

The basic physical and chemical ion-surface interactions are schematically shown in Fig. 3. When energetic inert-gas ions strike a surface a number of events can occur: (1) the particle may enter the surface and become trapped-implantation; (2) as a result of momentum transfer an atom from the surface can be ejected-sputtering, or (3) the impinging ion may be reflected from the surface and subsequently neutralized. In addition to the above processes, bombardment causes emission of secondary electrons which are essential to sustain the process.

The particle bombardment of surfaces depending on their energy level are generally considered as low energy particles when in the 1 to 10 keV range and high energy when >10 keV. The low energy particles are sufficient to cause sputtering and defect production, but the range of penetration into the bulk is limited to about few hundred atomic layers.

The chemical aspect of the activation energy for the process is provided by the reactive gas discharge. Chemical reactions are accelerated at a given temperature during reactive-ion bombardment and are the basis for ion nitriding, carburizing, and oxidation.

#### PLASMA ASSISTED DEPOSITION TECHNIQUES

**SPUTTERING** - The sputtering process is perhaps the most basic and relatively well characterized and understood and also the most widely used one. Sputter-deposition has become a generic name for a variety of sputtering processes. Of all the various sputtering processes, the dc-diode has the most simplistic configuration, which essentially consists of two metal electrodes placed about 5 cm apart in a vacuum chamber and backfilled with inert gas (argon) as schematically shown in Fig. 4. With this type of system, sputtered material can be transported from the target (cathode) to the substrate (anode) to form a film. The limitations imposed on this system are due to the relatively high gas pressure and the requirement that the target be a conductor. Because of electrical charge accumulation on the target surface, dc voltage cannot be transferred to insulating-nonconductive target materials. This difficulty can be overcome by replacing the dc applied voltage with RF (radiofrequency)

voltage at a high frequency usually at 13.56 MHz.

An RF discharge generated by a plane parallel electrode with capacitive coupling of the RF signal through a matching network results in large RF voltages and gas breakdown. Essentially the plasma is generated by the target RF electric fields. As a result, the sputtering of nonconductive materials (ceramics, polymers, etc.) is based on the principle that a self-bias voltage that is negative relative to plasma floating potential develops on any surface that is capacitively coupled to the glow discharge.

Another sputtering variant which is most widely used today involves the use of magnetic fields and is known as magnetron sputtering. The magnetic fields are usually applied by fixed permanent magnet pole pieces (several hundred gauss) in close vicinity to the target to produce several important modifications in the process as shown in Fig. 5. The target generated secondary electrons are trapped in cycloidal trajectories near the target and thus do not bombard the substrate. The magnetic field lines exit and reenter the cathode, forcing electrons into spiral motions along the field lines forming a magnetic tunnel where the electrons are trapped. Trapping of the electrons ensures increased plasma ionization. It should be pointed out that the magnetic field affects and directs the electrons but not the ions. The distinct advantages which arise from the electron trapment are the increased plasma ionization in the vicinity of the target, thus significantly increasing the sputtering rate, increasing activation for chemical reaction in the reactive mode, and preventing the electrons from bombarding the substrate which is the chief cause of heating in sputtering, especially important for coating heat-sensitive materials.

**ION PLATING** - Ion plating combines the high energy impingement of ions or energetic atoms of the implantation and sputtering processes, the high throwing power of electroplating, and the high deposition rates of thermal evaporation. There is a basic difference between sputtering and ion plating: in sputtering, the coating materials is usually generated by impact evaporation and transfer occurs by a momentum transfer process, in ion-plating, generation is by thermal evaporation and transfer is by an electric field acceleration. The ion plating is more energetic than the sputtering process, since a high substrate bias of several thousand volts accelerates the positively ionized evaporant atoms into the substrate. Basically, during ion plating the substrate and/or depositing film are subjected to a flux of high energy particles, which are sufficient to cause changes in the interfacial regions or films compared to nonbombarded deposition.

The basic ion-plating system consists of a dc-diode configuration, where the specimen is made the cathode of a high voltage dc circuit with an evaporation source as anode and is shown in Fig. 6

The interest in ion plating originates from its three unique features: (1) The flux of high energy particles contributes to a graded interface and the excellent adherence of the film and the desirable nucleation and growth kinetics (2) The high throwing power resulting from considerable atomic scattering provides for three-dimensional coverage to coat complex, intricate components without rotation (3) When used in the reactive mode, this flux provides activation energy to synthesize stoichiometrically uniform compound films such as TiN, Si<sub>3</sub>N<sub>4</sub>.

Since in diode ion plating systems the plasma is generated by the ionizing effect of secondary electrons ejected from the cathode, the ionization is relatively low. It has been estimated that under typical ion plating conditions (3 to 5 kV, argon pressure 20 mTorr cathode current density 0.3 to 0.6 mA/cm<sup>2</sup>) the ions carry only 10 percent of the energy dissipated while the energetic neutrals carry 90 percent. The energetic neutrals which are generated through charge transfer collisions constitute a very significant proportion of the energy carried. The ions and the activated neutrals may have a distribution of energies from thermal 0.2 eV up to the voltage applied to the discharge. Recently, enhanced plasmas have been used, the intensification being provided by auxiliary electron emission sources. The diverse range of modifications and designs are schematically shown in Fig. 7. All of the designs basically consist either of increasing the number of ionizing electrons, or making their trajectories longer, thus promoting increased ionization. These above configurations are generally referred to as triode ion plating systems. These processes have a distinct advantage, that the ionization enhancement, the ion current, can be controlled independently of the bias voltage and regulated independently from the evaporation rate. The triode ion plating systems are primarily used in the deposition of dense ceramic (nitride, carbide) coatings in the reactive mode.

#### PLASMA ASSISTED SURFACE MODIFICATION TECHNIQUES

The plasma assisted surface modification techniques can be further classified as Ion Beam Techniques (Ion Implantation, Ion Beam Mixing and Laser Processing) and Plasma Thermomechanical Processes (Ion Nitriding, Ion Carburizing, Plasma Oxidation).

#### Ion Beam Techniques

ION IMPLANTATION - Ion implantation is a nonequilibrium technique, practically free from thermodynamic constraints such as diffusivity and solubility. Essentially any ion can be implanted into any surface layer to a depth that is in principle determined by the ion energy and the characteristics of the material to be implanted, and the depth profile normally has a Gaussian distribution as shown in Fig. 8. Controlling the energy of the ions one controls the depth of penetration. Typical implantation energies range from 10 to 500 keV and give penetration depths in the range from 10 to 1000 nm. Typical fluences for nitrogen implantation range from 10<sup>16</sup> to 10<sup>18</sup> ions/cm<sup>2</sup> into steels or iron.

A typical ion-implantation system is schematically shown in Fig. 9. The material to be converted into ions is introduced as gas into the chamber, and by heating the filament, energetic electrons collide with the gas atoms ionizing them. The positive ions are then extracted through a slit, directed through magnetic field that performs mass analysis and selectively filters out all but the desirable ions. The current to the magnet determines which ions pass through the aperture. Thus only ions of single type and energy, namely a purified beam is produced and focused and accelerated to the high final energy to strike the target material. Since the beam is narrow, typically a few centimeters in diameter, it must be rastered across the surface of the target to be implanted. Ion implantation is an athermal and line-of-sight process.

ION BEAM MIXING - Since ion implantation generates relatively shallow depths of penetration, recently new hybrid techniques have been developed which combine both, ion implantation and vapor deposition referred as Ion Beam Mixing. This process is shown schematically in Fig. 10. In this process one has two alternatives (1) deposit either single or multiple film materials and subsequently expose the surface to ion bombardment as shown in Fig. 10 or (2) deposit the film simultaneously during ion bombardment. Ion induced mixing initiates a variety of film-substrate solid interactions such as mixed regions and phase transformations. In ion beam mixing the bombardment is generally performed by heavy ions with energies in the 100 to 500 keV range.

LASER PROCESSING - In recent years the laser processing techniques have achieved increasing acceptance for modifying the near-surface properties of materials. Basically two types of lasers are in use: the solid state and the gaseous lasers. The solid

state lasers use a solid material as its working medium, most common material is ruby. The gas lasers are primarily using CO<sub>2</sub> or in some instances argon. Further, these lasers can be categorized as pulsed or continuous wave lasers. Pulse durations are in order of 10<sup>-9</sup> to 10<sup>-15</sup>s.

Laser processing can be performed in either solid state (heat treatment, thermal anneal) or in liquid state (glazing, cladding, grain refinement, amorphous phase). The basic mechanism of laser glazing consists of surface melting and rapid solidification as shown in Fig. 11. When a high power laser is scanned over a surface with limited pulse duration (~10<sup>-9</sup> to 10<sup>-15</sup>s), only the near surface of the solid melts, and resolidification quench rates up to 10<sup>11</sup> K/s can be readily achieved. The precise control of these techniques makes it possible to vary and control the depth of surface melting. Thus the origins of new material properties are induced by surface melting and rapid solidification.

#### Plasma Thermochemical Processes

Ion nitriding, ion carburizing, or plasma oxidation are thermochemical processes where chemical reactions are accelerated at a given temperature in the presence of reactive ion bombardment in a discharge gas N<sub>2</sub> + H<sub>2</sub>, methane or oxygen respectively.

ION NITRIDING - Ion nitriding is a plasma thermochemical surface hardening technique where the specimen is the cathode of a dc glow discharge of N<sub>2</sub> and H<sub>2</sub> gas and schematically shown in Fig. 12. Impinging ions deliver enough kinetic energy to the specimen to heat it to a preselected nitriding temperature thus auxiliary heating is not necessary in many instances. The working pressure varies between 1 to 10 Torr and the applied dc voltage is between 300 to 800 V. The current necessary is a product of the total area under glow and the value of current density required to maintain it in the abnormal range. A convenient rule of thumb is 1 mA/cm<sup>2</sup>.

The basic reaction mechanism of ion nitriding has not been agreed upon yet. However, the two most commonly proposed explanations are: (1) based on ion bombardment where sputtered Fe reacts with atomic nitrogen in the gas phase, forming the unstable FeN, which after condensation on a surface releases atomic nitrogen as schematically shown in Fig. 13 or (2) adsorption of atomic nitrogen, where sputtering of Fe is not the controlling factor.

One basic question in all glow discharge processes is the degree of ionization. Very little is known how enhanced ionization would affect the diffusion processes such as in ion nitriding.

Some studies have been conducted where ion nitriding is performed in a low pressure intensified glow discharge (triode ion plating) in the 2x10<sup>-2</sup> Torr range. A comparison of typical hardness distribution results for a low content carbon steel (C < 0.05 percent) obtained in the

low pressure triode system versus the conventional high pressure diode system are shown in Fig. 14. A considerable increase in nitrogen penetration is observed if the triode ion plating system is used.

#### CONCLUDING REMARKS

The plasma assisted deposition/modification techniques have achieved increased acceptance in recent years both as tools for basic materials research and development and as techniques for industrial applications to modify the surface/subsurface properties of materials.

The criteria for selecting a particular technique depends primarily on the understanding of the basic principles of the operating mechanisms, coating, or modified surface/substrate interactions and the behavior between the modified surface and its environment during use.

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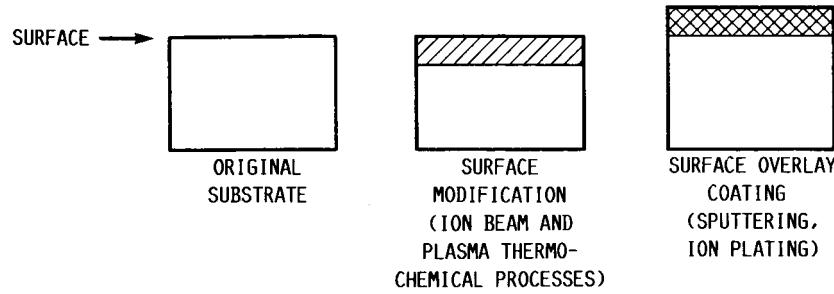


FIGURE 1.- SURFACE MODIFICATIONS.

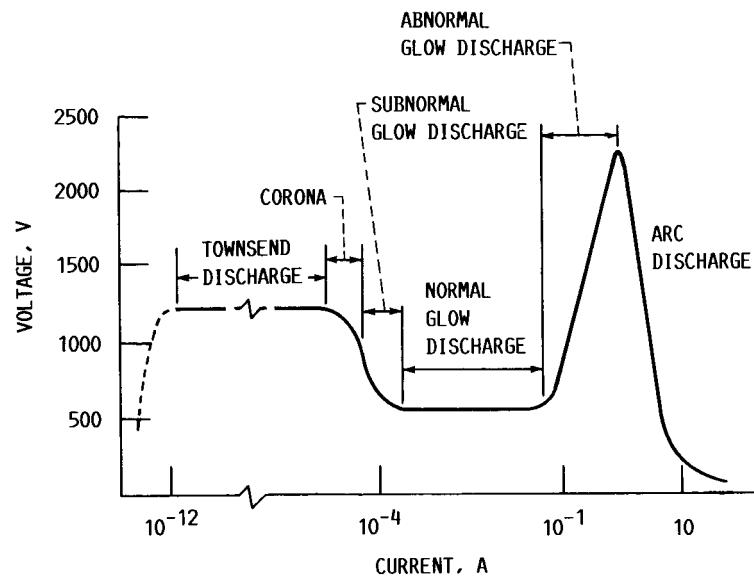


FIGURE 2.- VOLTAGE-CURRENT CHARACTERISTICS OF DIFFERENT TYPES OF DISCHARGE IN ARGON (EDENHOFER).

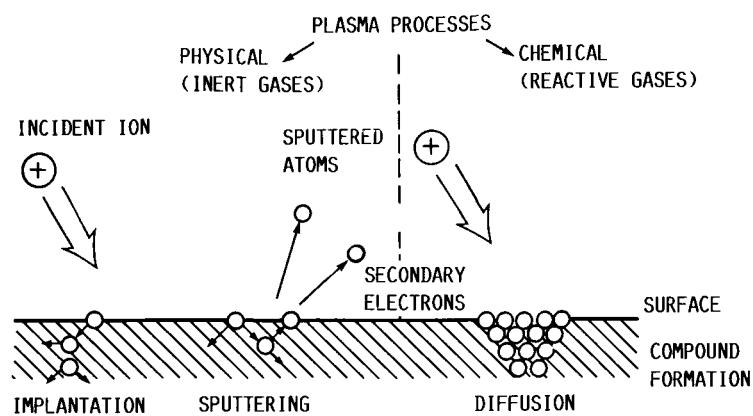


FIGURE 3.- ION - SURFACE INTERACTIONS.

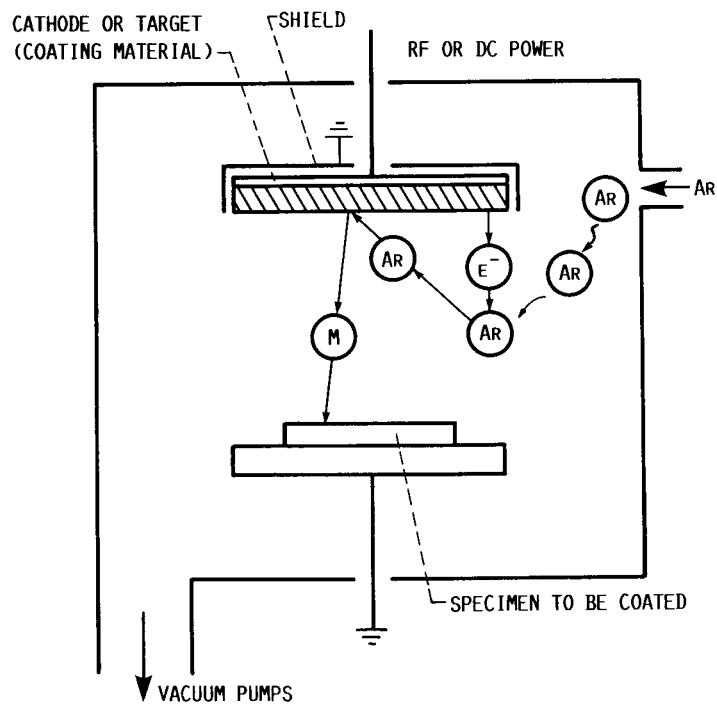


FIGURE 4.- MECHANISM OF SPUTTERING.

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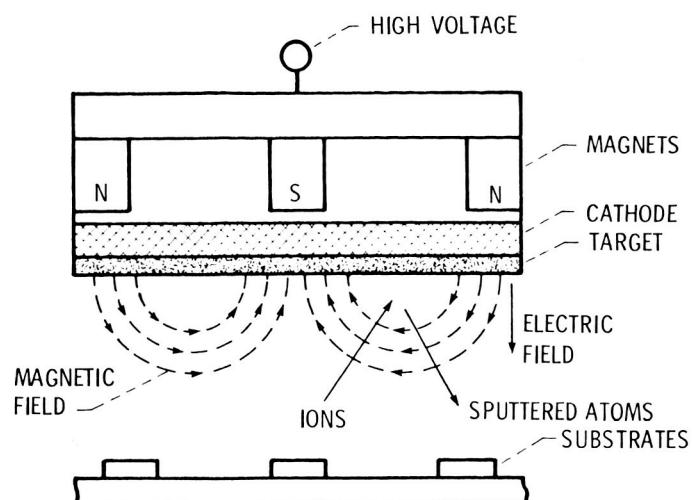
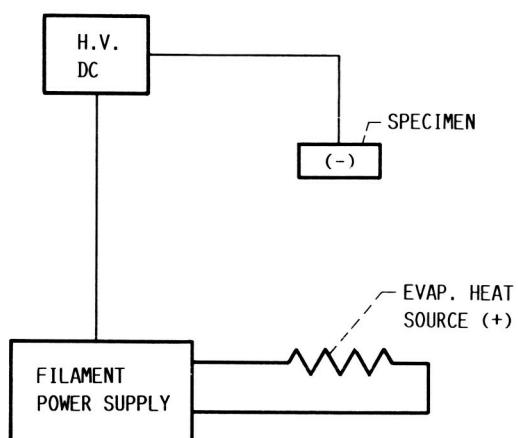
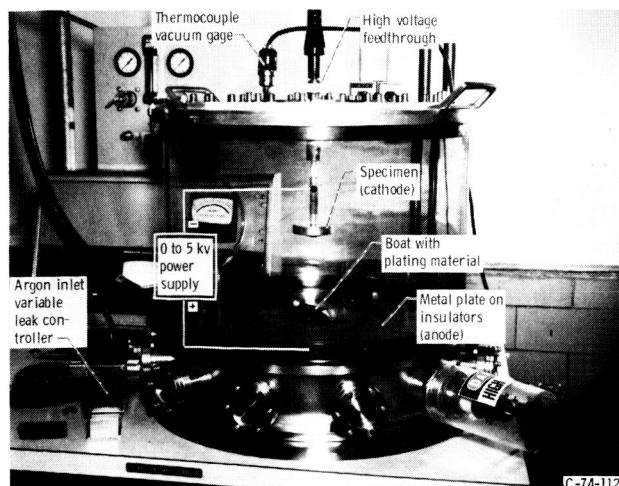


FIGURE 5.- MAGNETRON SPUTTERING CONCEPTS.



(A) SCHEMATIC.



(B) ION PLATING CHAMBER.

FIGURE 6.- ION PLATING SYSTEM.

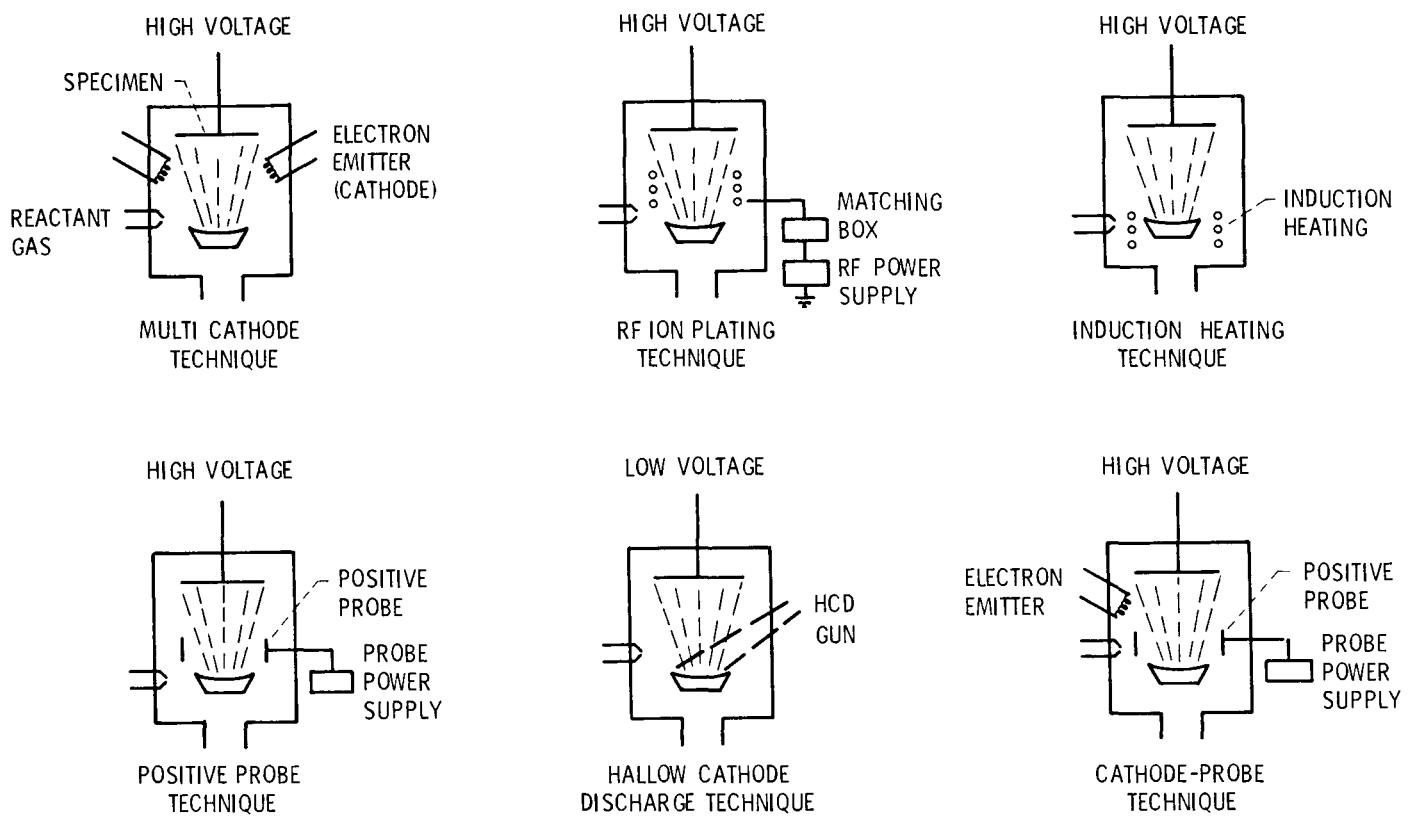


FIGURE 7.- ENHANCED IONIZATION TECHNIQUES OF ION PLATING.

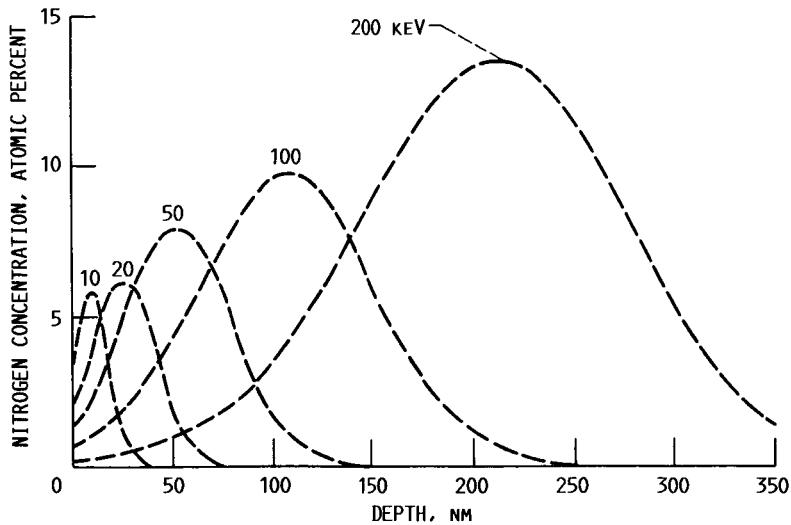


FIGURE 8.- DEPTH DISTRIBUTION OF NITROGEN IONS IMPLANTED IN IRON AT VARIOUS BEAM ENERGIES, KEV.

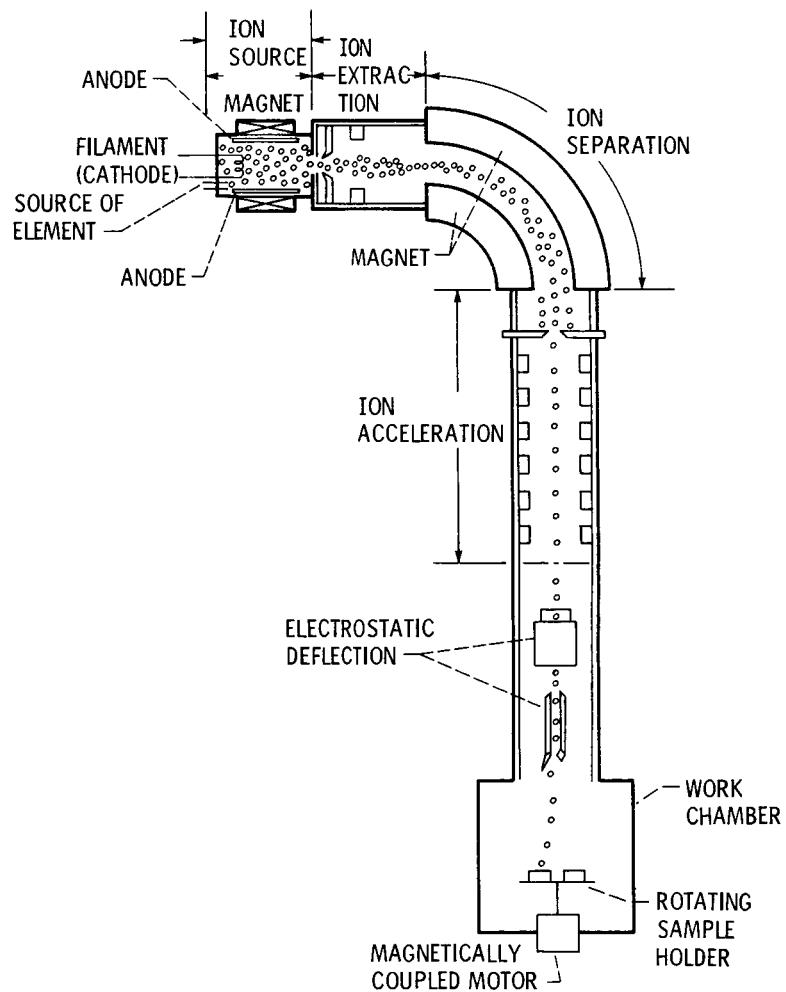


FIGURE 9.- TYPICAL ION IMPLANTOR.

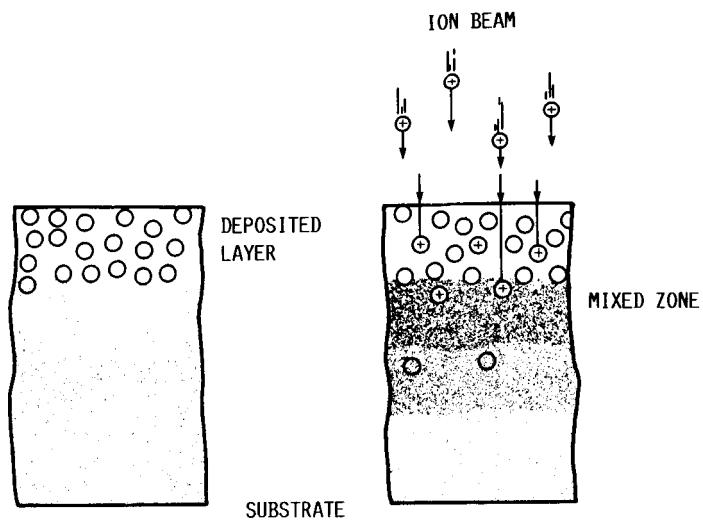


FIGURE 10.- ION - BEAM MIXING.

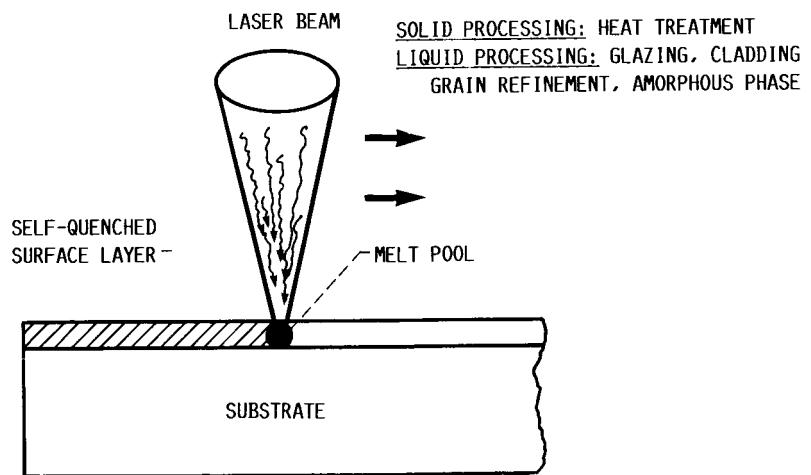


FIGURE 11.- LASER PROCESSING.

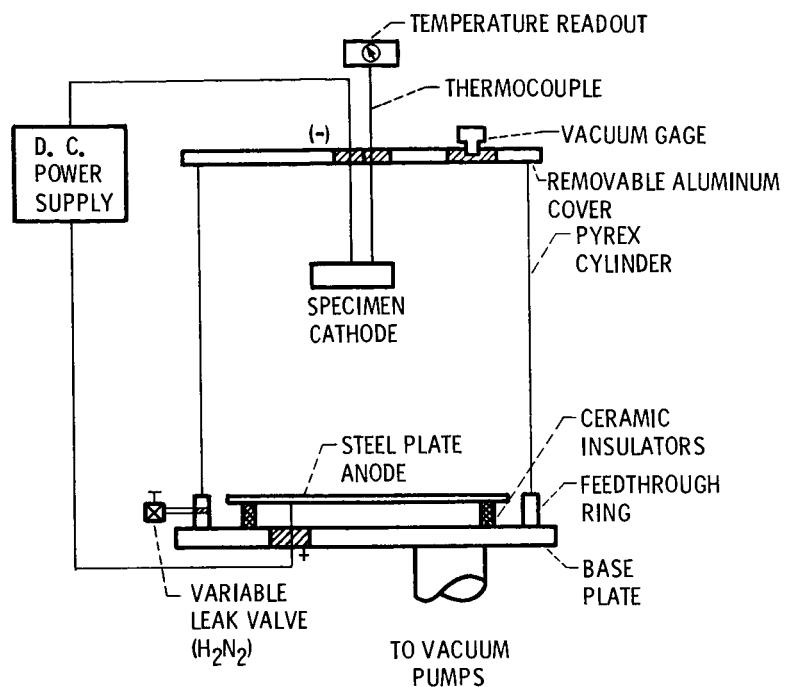


FIGURE 12.- SCHEMATIC OF ION NITRIDING SYSTEM.

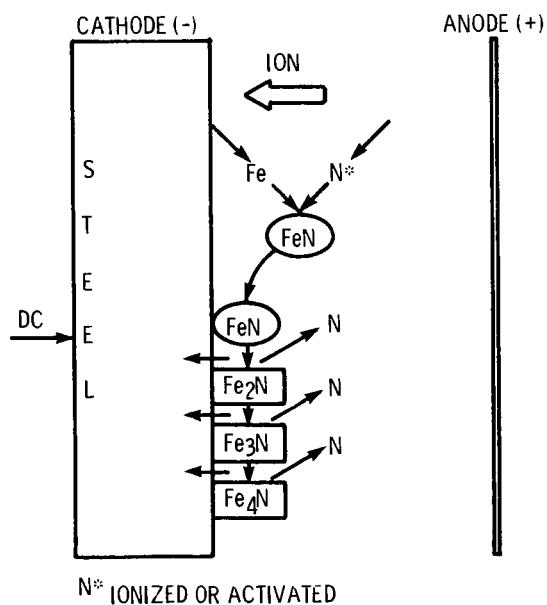


FIGURE 13.- GLOW DISCHARGE ION NITRIDING MECHANISM.

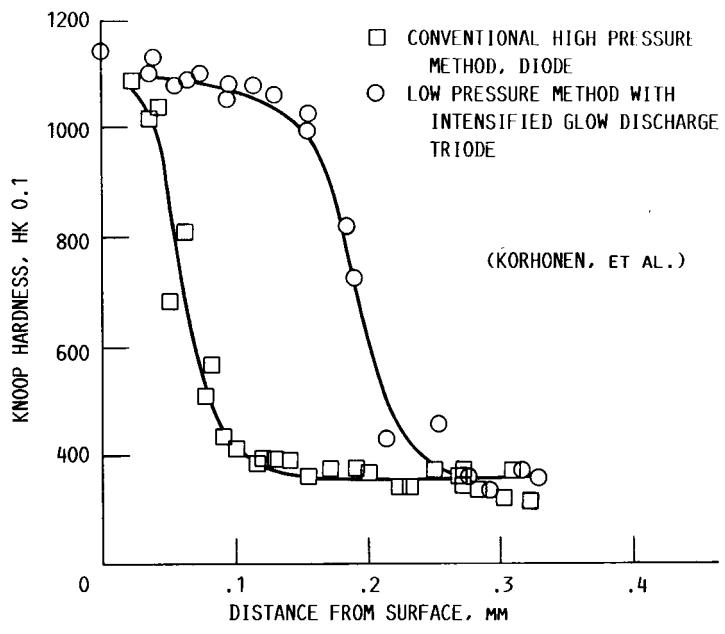


FIGURE 14.- HARDNESS DISTRIBUTIONS AFTER PLASMA NITRIDING  
NITRIDING OF A STEEL .05% C AND 4.4% CR AT 450

1. Report No. <b>NASA TM-88885</b>	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle  <b>Plasma Assisted Surface Coating/Modification Processes: An Emerging Technology</b>		5. Report Date	
		6. Performing Organization Code <b>506-43-11</b>	
7. Author(s) <b>Talivaldis Spalvins</b>		8. Performing Organization Report No. <b>E-3274</b>	
		10. Work Unit No.	
9. Performing Organization Name and Address  <b>National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135</b>		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address  <b>National Aeronautics and Space Administration Washington, D.C. 20546</b>		13. Type of Report and Period Covered <b>Technical Memorandum</b>	
14. Sponsoring Agency Code			
15. Supplementary Notes  <b>Prepared for the First International Ion Nitriding Conference, cosponsored by the American Society for Metals and NASA Lewis Research Center, Cleveland, Ohio, September 15-17, 1986.</b>			
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17. Key Words (Suggested by Author(s))  <b>Sputtering; Ion plating; Ion implantation; Ion nitriding</b>		18. Distribution Statement  <b>Unclassified - unlimited STAR Category 31</b>	
19. Security Classif. (of this report) <b>Unclassified</b>	20. Security Classif. (of this page) <b>Unclassified</b>	21. No. of pages	22. Price*